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San Joaquin Valley Drainage Program

TECHNICAL REPORT

SEPTEMBER 1988

AGRICULTURAL DRAINAGE WATER TREATMENT, REUSE, AND DISPOSAL IN THE SAN JOAQUIN VALLEY

PART I
TREATMENT TECHNOLOGY

The San Joaquin Valley Drainage Program was established in mid-1984 as a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the Program are to investigate the problems associated with the drainage of irrigated agricultural lands in the San Joaquin Valley and to formulate, evaluate, and recommend alternatives for the immediate and long-term management of those problems.

This report is one of several Program technical reports presenting research findings to date and implications on specific topics such as geohydrology of the San Joaquin and Tulare Lake Basins, fish and wildlife resources, public health, agricultural setting, planning methods, and drainage water treatment, reuse, and disposal. The data and information in these reports are being used in formulating and evaluating drainage water management options and preliminary alternative plans, which will be presented in a separate report in late 1988. A draft report outlining latest study results and alternative plans will be completed for public review in the fall of 1989. Final study results and recommended area-specific plans will be presented in the Program's final report in the fall of 1990.

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TECHNICAL REPORT

AGRICULTURAL DRAINAGE WATER TREATMENT, REUSE, AND DISPOSAL IN THE SAN JOAQUIN VALLEY OF CALIFORNIA

PART I: TREATMENT TECHNOLOGY

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SUMMARY AND CONCLUSIONS

The means for treatment and removal of undesirable salts and trace elements from subsurface drainage water are not currently available at a price that agriculture will pay. Whereas the removal of salts is a well-developed technology, it is very expensive. The reduction of trace elements, particularly selenium, presents major problems. Many processes have been screened and several promising ones are now under investigation. There have been promising results from laboratory bench tests and small scale pilot plant studies, but no single process has been developed to a stage where the technology can be transferred to large prototype operation.

At this time, investigations of treatment processes related to San Joaquin Valley agricultural drainage water can be summarized as follows:

1. Biological Treatment

The anaerobic bacterial treatment process (Binnie California, Inc.) tested in a pilot plant has demonstrated ability to reduce selenium in drainage water. A sludge blanket reactor appears to be the most effective biological system. Drainage water containing 300-550 ug/L of selenium can be reduced to about 10-40 ug/L, after microfiltration. After polishing in boron selective ion exchange resins, the selenium can be reduced to less than 10 ug/L. Boron can be reduced from about 10 mg/L to less than 1 mg/L. According to Binnie, treatment costs in a prototype plant (1 Mgal/d) will be about $76/acre-foot to construct and about $148/acre-foot to operate

(total $224/acre-foot). A larger plant (10 Mgal/d) is estimated to reduce unit treatment estimates for construction and operation to about $145 to $175/acre-foot, depending on available carbon source. These costs do not include disposal facilities. Continuation of development at prototype plant scale is being considered by Westlands Water District.

The microalgal/bacterial treatment process has shown developmental progress under Professor W. J. Oswald of the University of California. Algal biomass grown in a pilot high rate ponds has been harvested and digested for production of reductant sludge material and methane. The reductant has shown capability in laboratory studies to reduce selenium from 359 ug/L down to 20 ug/L. Further reduction can be expected in a final air flotation system. Methane yield from digesters was over 0.29 L/gm of volatile solids and can provide energy to the process facilities, with surplus electric power. Further work is in progress to define the process and to provide detailed cost estimates.

The ability of facultative bacteria to reduce selenium has been demonstrated by the Bureau of Mines studies (P. Altringer). These preliminary studies were conducted with bench scale biological reactors. Further studies are under way to identify the bacterial process and related kinetics. If the bench scale results are promising, larger reactors should be constructed in the laboratory or in the field to pursue process development. The process could be less costly than others, since open reactors can be used, with reduced capital investments.

In-situ biological processes are under study for the cleanup of Kesterson Reservoir. The University of California, Lawrence Berkeley

Laboratory, is studying the immobilization of selenium in pond sediments. Professor W. Frankenberger of the University of California, Riverside is studying the volatilization of selenium from soil systems. Both the immobilization and volatilization processes have been demonstrated in the laboratory and at the site. Studies are still under way to better understand these processes and any limitations to large scale applications. The biochemistry and geochemistry of these processes need to be defined along with the kinetics and ecological consequences. Work is continuing at this time on both the volatilization and immobilization processes.

2. Chemical Treatment

The Denver Office of the U.S. Bureau of Reclamation has been investigating the use of ferrous hydroxide as a reductant to convert selenate to lower soluble forms for removal. Studies have been conducted at laboratory and field level using static reactors. Preliminary information indicates that selenium can be reduced in this process to less than 5 ug/L. The chemistry of the process is influenced by the dissolved oxygen and nitrates in the drainage water. Consequently, treatment costs are related to the chemical dosage and the reaction time required to lower nitrates and oxygen before selenium can be reduced to lower solubility states. Work is still in progress to optimize the process and related costs. If shown to be promising, pilot plant testing would be in the next stage of development.

3. Physical Adsorption

The ability to remove selenium from drainage water with iron filings has been demonstrated by the Harza Process at the Panoche Drainage

District. The reduction level is dependent on bed overflow rate and the contact time in the iron filing beds. Preliminary studies indicated a cost range from $70 to $285/acre-foot, which is dependent on bed life and selenium removal expectancies. Bed life is an important factor since clogging has been a major problem. The cause of clogging and possible remedial measures have not been determined but studies are under way by Harza Engineering Company. Construction of a pilot plant for continuous operation at selected drainage sites is being considered by Harza Engineering and the Panoche Drainage District to determine the feasibility of the process including better estimates of bed life.

The development of selenium selective resins has been under study by Boyle Engineers. Initial studies with selected commercial resins have indicated selective trends for selenate over sulfate. Further work will be needed to enhance these selective characteristics with commercially available resins.

4. Reverse Osmosis

Various methods of desalination have been developed, mainly for large scale desalting of seawater. Most are energy intensive and costly, probably beyond the affordability of the agricultural economy of the west side of the San Joaquin Valley. Reverse osmosis (RO) is considered the best technology for desalination of drainage water. Studies were conducted by the California Department of Water Resources at their Los Banos desalting facility from 1982 to 1986 and a report on their findings is due in 1988. In 1985, the SJVDP funded a study by CH2M Hill consultants to evaluate the use of off-the-shelf RO technology. A three-stage RO process

was evaluated to recover up to 87 percent of the feedwater, so that reject brine disposal would be less costly. CH2M Hill concluded that the TDS of the product water would be 550-650 mg/L, that selenium levels would be reduced to 10-20 ug/L and that boron would be reduced to 7-8 mg/L. The treatment cost for their selected process train was $1,090/acre-foot, not including cost for brine disposal. If California Class I ponds were required for disposal of the brine stream, the total cost would be $1,650/acre-foot. However, if Class II ponds could be used, the total cost would be $1,140/acre-foot. The reuse of product water remains an option but may be limited by the projected chemical characteristics and intended use.

5. Cogeneration Systems

The technology for cogeneration /evaporation/crystallation has potential for management of drainage water. Byproducts can include electricity, water for reuse, and salts. The application of this technology is under assessment for further development.

During FY 1989, the SJVDP intends to continue development work on the more promising treatment processes. Further work on select processes will depend on outcomes of current studies while State and local agencies will support other promising processes.

PART I

TREATMENT TECHNOLOGY

INTRODUCTION

The contamination due to trace elements in San Joaquin Valley agricultural drainage water reported at Kesterson Reservoir, in Merced County, California, has emphasized the need for a new treatment technology as a part of a comprehensive plan to solve the drainage problem. One of the basic goals of the San Joaquin Valley Drainage Program (SJVDP), and local and State interests is to seek affordable methods that can remove contaminants from drainage water so that the quality of receiving waters and their beneficial uses can be protected.

Various treatment methods that could solve the San Joaquin Valley drainage problem were screened. The more promising processes are being examined to evaluate and compare their effectiveness, operational problems, and costs. The status of these investigations are reported here as a technical report of the San Joaquin Valley Drainage Program.

TREATMENT OBJECTIVES

Contaminants and pollutants that may be found in the San Joaquin Valley drainage water are a critical part of the development and the evaluation of treatment technology. A typical drainage water analysis shows its complex chemical characteristics (see table I-1). The table presents results of analyses from samples taken from the San Luis Drain

TABLE I-1

Water Analysis
San Luis Drain at Mendota
(SLDC 41)

Constituent[1]	Units	Average	Maximum	Standard Deviation
Sodium	ppm	2230	2820	200
Potassium	ppm	6	12	1
Calcium	ppm	554	714	25
Magnesium	ppm	270	326	20
Alkalinity (as $CaCO_3$)	ppm	196	213	10
Sulfate	ppm	4730	6500	400
Chloride	ppm	1480	2000	100
Nitrate/nitrite (as N)	ppm	48	60	5
Silica	ppm	37	48	4
TDS	ppm	9820	11600	500
Suspended solids	ppm	11	20	3
Total organic carbon	ppm	10.2	16	3
COD	ppm	32	80	8
BOD	ppm	3.2	5.8	1.0
Temperature[2]	deg C	19	29	-
pH	-	8.2	8.7	0.2
Boron	ppb	14400	18000	2000
Selenium	ppb	325	420	90
Strontium	ppb	6400	7200	500
Iron	ppb	110	210	50
Aluminum	ppb	<1	<1	-
Arsenic	ppb	1	1	-
Cadmium	ppb	<1	20	-
Chromium (total)	ppb	19	30	-
Copper	ppb	4	5	-
Lead	ppb	3	6	-
Manganese	ppb	25	50	-
Mercury	ppb	<.1	<.2	-
Nickel	ppb	14	26	-
Silver	ppb	<1	<1	-
Zinc	ppb	33	240	-

NOTES:

[1]Average and maximum data from "San Luis Drain, Inflow and Water Quality Data," Table I, USBR June 1985. Standard Deviation by consultant CH2M Hill (1986).

[2]Temperature varied from 23-25 deg C summer to 12-15 deg C winter. Minimum water temperature over 4-year date span was 7 deg C.

near Mendota and represents a mix of water from the major drains. This water is shown to be high in salinity (TDS), sulfate, calcium, chloride, and sodium as well as selenium, boron, and other constituents. These characteristics pose difficult challenges for the removal of salts and trace elements.

Based on occurrence in drainage water on the west side of the San Joaquin Valley and their importance in terms of water quality objectives, the following substances of concern have been identified for studying and problem solving purposes: salinity, arsenic, boron, chromium, mercury, molybdenum, and selenium. Other substances of interest include aluminum, cadmium, copper, lead, lithium, manganese, nickel, silver, vanadium, and zinc because of their water quality significance to beneficial uses and public health. However, the SJVDP treatment technology studies have been focused on the removal of salinity, and selenium at this time. Salinity reduction is seen to be a major goal for maintaining the salt balance in the valley. Selenium has been identified as a cause for biological damages at Kesterson Reservoir. Moreover, it is seen as the most difficult trace element for treatment and therefore must be investigated as a priority. It is to be noted that treatment processes that reduce the concentration of any one of these substances under study may also reduce other trace elements and these encompassing capabilities will be considered as part of the evaluation of each treatment process.

The adoption of water-quality objectives is a complex process that seeks to define the limits or levels of water-quality constituents or

characteristics to reasonably protect the beneficial uses of specific water bodies. These objectives define the waste discharge requirements or constituent limits and the design criteria or goals of treatment processes. With regard to water quality objectives and substances of concern, the California State Water Resources Control Board (SWRCB) Technical Committee (1987) reviewed data on (1) Water quality criteria, and (2) concentrations in drainage water for 26 quality-degrading constituents in subsurface drainage water that may be discharged to the San Joaquin River. It selected from this list four constituents--salinity, selenium, boron, and molybdenum--representing those which the committee concluded to be of greatest concern. In August 1987, the SWRCB approved the Technical Committee Report, which recommended water quality objectives in the San Joaquin River Basin as shown in table I-2. These recommendations were forwarded to the Central Valley Regional Water Quality Control Board to adopt appropriate basin plan amendments and implement a program to regulate agricultural drainage flows in the San Joaquin Basin. Because agricultural drainage is the major source of pollutants, the objectives recommended by the SWRCB become the focus for agricultural drainage control measures. However, the SJVDP treatment technology efforts, to date, have been directed mainly to removing selenium and to desalination.

TREATMENT TECHNOLOGY REVIEW

The treatment of agricultural drainage is a technical and economic challenge. Review of the technical literature does not reveal real experiences in the management of large volumes of agricultural drainage

TABLE 1-2

RECOMMENDED
WATER QUALITY OBJECTIVES
FOR THE
SAN JOAQUIN RIVER BASIN [2/]

LOCATION	CONSTITUENT	MAXIMUM MEAN MONTHLY LEVEL	INSTANTANEOUS MAXIMUM	COMPLIANCE DATE
Interim Objectives				
San Joaquin River at Hills Ferry and downstream	Selenium	5 ppb	26 ppb	October 1991
Grassland WD, San Luis NWR and Los Banos SWA	Selenium	2 ppb (can be provided via a substitute supply) [1/]		October 1989
Long-term Objectives				
San Joaquin River at Hills Ferry and downstream	Selenium	To be determined based on site-specific data		To be determined
	EC	1.0 mmho		
	Boron	700 ppb	5,800 ppb	
	Molybdenum	10 ppb	440 ppb	
Salt & Mud Sloughs & San Joaquin River Lander Ave. to Hills Ferry	Selenium	10 ppb	26 ppb	To be determined
Salt Slough and San Joaquin River Lander Ave. to Hills Ferry	EC	3.0 mmhos		To be determined
	Boron	2,000 ppb	5,800 ppb	
	Molybdenum	10 ppb	440 ppb	
Grassland WD, San Luis NWR and Los Banos SWA	Selenium	To be determined based on site-specific data (can be provided via a substitute supply) [1/]		To be determined

[1/] If a substitute supply of 2 ppb or lower is provided, the quantity of this supply should be in a volume equal to the lesser of either (1) the quantity of water (mid-1970's) diverted by these waterfowl areas or (2) the actual flow in the canals available to these areas.

[2/] SWRCB (1987).

containing both high salt loads and toxic trace elements. Therefore, an advanced technology must be developed, starting with basic laboratory research followed by pilot testing in a development process leading to practical field applications. Conventional wastewater treatment technology cannot effectively remove substances to meet the stringent requirements for toxic substance removal that have been recommended for receiving water quality objectives. New approaches and processes must be developed.

Numerous ideas for treatment of municipal and industrial wastewater have been reviewed for possible application to agricultural drainage water treatment. A list of desalination and trace element removal technologies that could potentially be applied to drainage water is shown in table I-3. This list was reviewed to select treatment methods with the best potentials for the development of viable processes.

The SWRCB Technical Committee studies prepared pursuant to their Water Quality Order 85-1 of 1985, for revising the water-quality objectives for the San Joaquin River Basin, provided a basic assessment of the treatment technology for drainage water. In this effort, the Technical Committee contracted with the Western Consortium for Health Professionals, Berkeley, to assess technologies that may be effective in achieving the committee's contemplated water quality objectives. Professor David Jenkins[1] (1987) prepared the technical assessment report. Because Jenkins' report presents, at this time, the most current assessment of trace element

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1. Prof. David Jenkins, Professor of Sanitary Engineering, University of California, Berkeley.

Table I-3. Potential Technology for Drainage Treatment

I. TRACE ELEMENT TREATMENT

Biological Treatment

Bacterial
Fungal
Microalgal Bacterial
Aquatic Systems
Agroforestry

Chemical Treatment

Iron Hydroxides
Alum
Lime Soda
Sulfides

Physical Adsorption

Iron Filings
Ion Exchange Resins
Activated Carbon
Activated Alumina

Electrochemical Treatment

Electrolytic Reduction/Coagulation
Electron Exchange Resins

II. DESALINATION

Reverse Osmosis
Evaporation
Electrodialysis
Freeze Crystallization
Vapor Compression
Ultrafiltration
Ion Exchange

treatment methods for application to drainage, excerpts have been taken almost verbatim and included as an appendix to this report (Appendix A) as a background information document.

Jenkins reviewed the basic technology for biological, chemical, adsorption, and ion exchange treatment methods for the removal of trace elements. The following salient points are summarized from his technology assessment for the treatment of drainwater to reduce concentrations of selenium, boron, and molybdenum.

Selenium

1. Agricultural drainage water from the San Joaquin Valley presents a complex matrix for selenium removal because: (a) The selenate form dominates and is most difficult to remove, (b) the background levels of other chemicals, particularly sulfate, dominate in massive proportions, and (c) nitrates are present in high levels and must be reduced before selenate reduction can be achieved.
2. Most chemicals used in treatment processes are not expected to remove selenium to the 2-5 ug/L levels proposed for receiving waters objectives.
3. Processes involving redox reactions appear to be the most promising for selenate reduction.

4. The iron filing process has demonstrated capability to reduce selenium at low application rates. There are problems reported in the cementation of the contact beds in field studies at the Panoche Drainage District.
5. The microbial catalyzed reduction of selenate has been reported from experiments at Murrieta Farms near Mendota, California. Anaerobic reactors and microfiltration can produce an effluent level of 10-40 ug/L. Polishing with ion exchange resins can further reduce selenium to less than 10 ug/L.
6. Anaerobic reactors other than fixed film (rocks) should be investigated, since clogging and flow distribution problems have been reported in denitrification studies with drainage. Fluidized beds and sludge blanket reactors should be studied to overcome these problems.
7. The biological uptake of selenium by algae occurs at levels which could not be developed into a process that would meet the objectives of agricultural drainage discharges. However, digested algae materials for reducing selenium in drainage are under current study.

Boron

1. Boron has been removed successfully from agricultural drainage water with selective resins already in commercial use.

Molybdenum

1. Methods for molybdenum removal have been under development in the mining and mineral processing industry. Chemical treatment with ferric hydroxide at low pH and selective ion resins can be effective, but these have not been evaluated in agricultural wastewater in the San Joaquin Valley.

Desalination technology has been developed over several decades through needs in seawater conversion for drinking water supplies in arid areas and for industrial demands. Various desalination methods are shown in table I-3 and a review of the technology has been included in Appendix B. The review by PRC Toups (1982) is informative and is the basis of the presentation in Appendix B. The technology that can provide the best potential for the desalination of drainage water is Reverse Osmosis (RO), although evaporation by flash distillation can have specific application. Both of these processes have been used for desalination in field applications on a worldwide basis.

TREATMENT PROCESS SCREENING

In the early stages of the SJVDP, numerous proposals and ideas to help resolve the San Joaquin Valley agricultural problems were received. Over 150 "unsolicited proposals" were received, a number of which contained proposals or suggestions for treating of drainwater to remove selenium. The SJVDP staff, working with the Interagency Technical Advisory Committee (ITAC) and the Treatment and Disposal Subcommittee, initially reviewed about 27 proposals, considered the most promising of the 150

received for development in drainage treatment. These proposals were further screened to derive a list for guiding developmental work, using the following screening criteria:

General Screening

1. Does the proposed study or action meet the needs of the interagency drainage team? If not, reject.
2. Does the proposed study duplicate work that has been, is being, or will be done by members of the interagency group or its contractors? If yes, reject.
3. Has the proposed study been submitted to other agencies outside the interagency group for funding? If yes, what is the status of other funding?
4. Do the technical backgrounds and qualifications of the principals indicate that they are capable of performing the work described? If not, is more information needed?
5. Does the proposal contain adequate descriptions of the test rationale and methods to reach a conclusion regarding its chances for success? If not, should more information be requested?
6. Does the proposal appear fundable using the U.S. Department of Interior (USDI) guidelines for unsolicited proposals (i.e., need for sole-source contract)?

Treatment Technology Screening

1. Is the process a demonstrated technology or is considerable research and development work required?

2. Based on scientific, engineering, social, and economic information, does the proposal appear feasible?
3. Is the proposed test scale adequate to demonstrate feasibility?
4. If the process is feasible, are the removal levels adequate (i.e., will the levels meet anticipated effluent limitations)?
5. Does the process description appear to cover all aspects of the system (e.g., sludge handling, additional ponds, etc.)?
6. What is the design capacity of the proposed process, and, if limited, what are the chances for increasing capacity?
7. Do treatment costs appear reasonable?
8. Any undesirable environmental impacts anticipated?

Based on the screening process in 1985 , the SJVDP staff and the ITAC Treatment and Disposal Subcommittee selected the most promising methods, for investigation and development for the removal of trace elements in drainage. In addition, assessments of desalination methods were also considered as part of a broad approach to the drainage treatment problem. These processes were identified as follows:

Trace Element Treatment

1. Biological Methods
   - o Anaerobic bacterial treatment
   - o Microalgal/bacterial treatment
   - o Aerobic/facultative bacterial treatment
   - o In-situ biological processes

2. Chemical Treatment
    - o Ferrous hydroxide
    - o Other chemicals
    - o In-situ physical-chemical attenuation
3. Physical Adsorption
    - o Iron filings
    - o Ion exchange resins
4. Electrochemical
    - o Electrocoagulation
    - o Electron exchange resins

Desalination

Reverse Osmosis

STATUS OF TREATMENT TECHNOLOGY STUDIES

Beginning in 1985, the SJVDP invested Federal funds in investigations of drainage treatment processes. In addition, studies have been funded and conducted by State and local water agencies. In a research and development process, these studies initially involve literature reviews and laboratory bench-scale evaluations to assess process effectiveness, as a prerequisite for proceeding with small-scale batch or continuous flow reactors. If success is attained, field-scale minisystems are operated to develop technical data for pilot prototype systems, wherein technical feasibility and costs are evaluated. Status of these studies and progress to date are described in the following paragraphs.

Biological Treatment

Anaerobic bacterial treatment. EPOC Agricultural Corporation of Fresno (now Binnie California, Inc.) studied anaerobic bacterial systems for the removal of selenium from water in their laboratory at London, U.K. and in a small-scale pilot plant located on Murrieta Farms near Mendota, California. Professor Jenkins (1987) prepared an assessment of the studies at Murrieta Farms (see Appendix A). Subsequently EPOC (1987) prepared and released a report on its investigations, covering a 2-year period (1985-1987) and related findings. A performance evaluation was made on the plant and a report was prepared by Binnie California Inc. (1988) in cooperation with the California Department of Water Resources. This evaluation covered the operational period February-March 1988. During the test period, the research work was financially supported by Murrieta Farms, California Department of Water Resources (DWR), Department of Fish and Game (DFG), State Water Resources Control Board (SWRCB), Westlands Water District (WWD), and EPOC resources.

The pilot plant process is composed of biological reactors, microfiltration facilities, and ion exchange units for the treatment of water to remove selenium and boron. A schematic flow diagram of the pilot plant is shown in figure I-1. Several types of biological reactors were studied, including upflow fixed-film beds (gravel and steel wool), fluidized beds (sand), and sludge blanket reactors. These reactors were operated under different flow configurations and fed either commercial methanol or a waste from sugar beet refineries (Steffan's liquor). Final

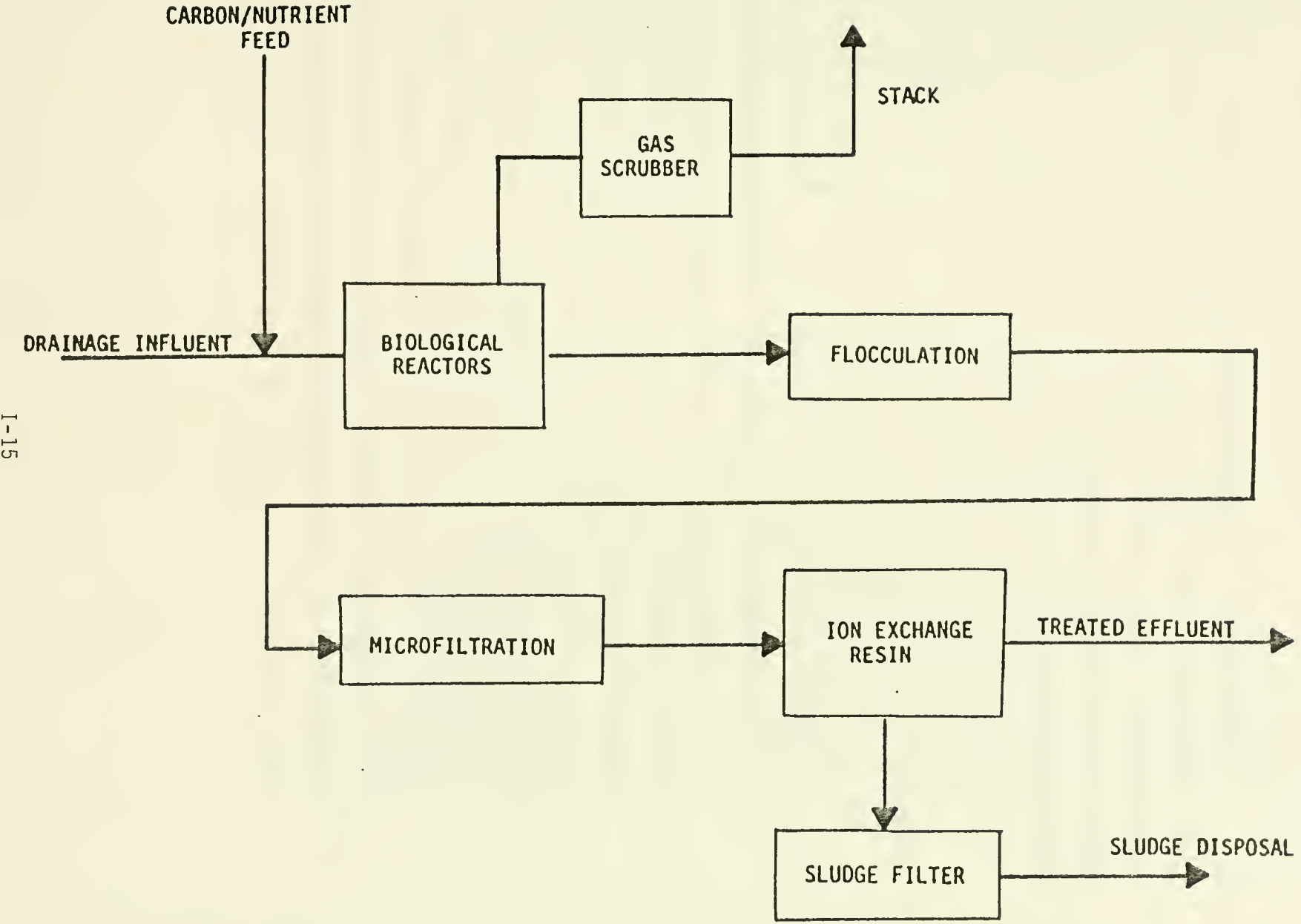


Figure I-1. Anaerobic bacteria treatment plant.

polishing processing included either ion exchange resins or a soil column filtration unit.

The Binnie evaluation report indicated that the biological reactors can reduce selenium from a drainage inflow containing about 300-550 ug/L to about 16-50 ug/L and, after the microfiltration process, to 10-40 ug/L. After polishing in the ion exchange resin or soil column, the selenium in the processed water was reduced to less than 10 ug/L. For the ion exchange process, boron was reduced from about 10 mg/L to less that 1 mg/L.

The following salient points were contained in the conclusions of the anaerobic bacteria treatment reports of EPOC and Binnie:

- o The biological process is a practical and proven method for the treatment of selenium laden drainage.
- o Biological growths in the reactors should be dispersed, rather than on fixed-films, to gain optimum design performance.
- o A pilot prototype plant (1 Mgal/d) was recommended to obtain engineering design data and operational details on the biological reactors, microfiltration system, and solar salt works.
- o The prototype (1 Mgal/d) is estimated to cost about $76 per acre-foot to construct and about $148 per acre-foot to operate (total $224 per acre-foot). This does not include disposal costs.
- o For a larger plant (10 Mgal/d), the scaling up of the basic plant will reduce the unit treatment cost estimates to about $145 to $175 per acre-foot. This does not include disposal costs.

- Recovery of salts and chemical byproducts can help in lowering disposal and overall treatment costs.

At present, a pilot prototype plant is under design by Binnie California for possible funding support of Westlands Water District. Detailed studies of treatment effectiveness under varying operational conditions will be an important finding expected from these new pilot plant studies. In addition, cost estimates can be improved from data gained from the construction and operation of the larger prototype plant. This information can add to the present state of the art for the process, particularly in regard to costs since the best estimates of this process to date ($145 to $175/acre-ft) are believed to be low when compared to data on existing advanced wastewater systems (EPA, 1984). At present (June 1988), the Westlands Water District has the proposal for the new plant under evaluation and has not made a final decision to proceed.

The U.S. Bureau of Reclamation and DWR have funded research by Professor Edward Schroeder at University of California, Davis on the microbial removal of selenium. A main objective of this project was to conduct laboratory-scale studies of anoxic packed-bed microbial reactors of the type used by Binnie California. Other objectives included determination of the potential of the mode of treatment, constraints on process operation, determination of the types or groups of organisms involved, and the end products of the reaction process. Schroeder (1987) concluded in his report that:

1. A substantial fraction of the SeO_4^{-2} in San Joaquin agricultural drainage water is quickly assimilated by microbial cultures naturally occurring in treatment units.
2. The remaining SeO_4^{-2} is apparently converted to Se^0 but the mechanism for this conversion is unclear at the present time.
3. Removal of the Se^0 by physico-chemical treatment procedures may be practical.
4. Chemical reduction of SeO_4^{-2} to Se^0 using a strong reducing agent should be investigated.
5. More complete understanding of the microbial processes involved in selenium removal is required if potential performance of biological treatment is to be established.

The SJVDP funded further research by Professor Schroeder in 1988 to:

1. Conduct continued study of the bacterial population of the pilot units with the objective of determining the mechanisms of selenium removal.
2. Investigate the role of redox potential in conversions of selenate (SeO_4^{-2}) to elemental selenium (Se^0).
3. Investigate the potential of assimilation as a principal removal mechanism.

These studies are presently in progress to provide a better understanding of the biochemistry and the bacteriology of the process. Work is scheduled for completion in late 1988.

Microalgal/bacteria treatment. Professor William Oswald and his team of researchers at UC, Berkeley have been conducting studies under cooperative agreements on a microalgal bacterial process. The process studied does not rely on either the direct algal uptake of selenium or the precipitation of selenium in the high-rate algal ponds. A literature survey and an assessment of the process was completed by Oswald (1985) for the SJVDP.

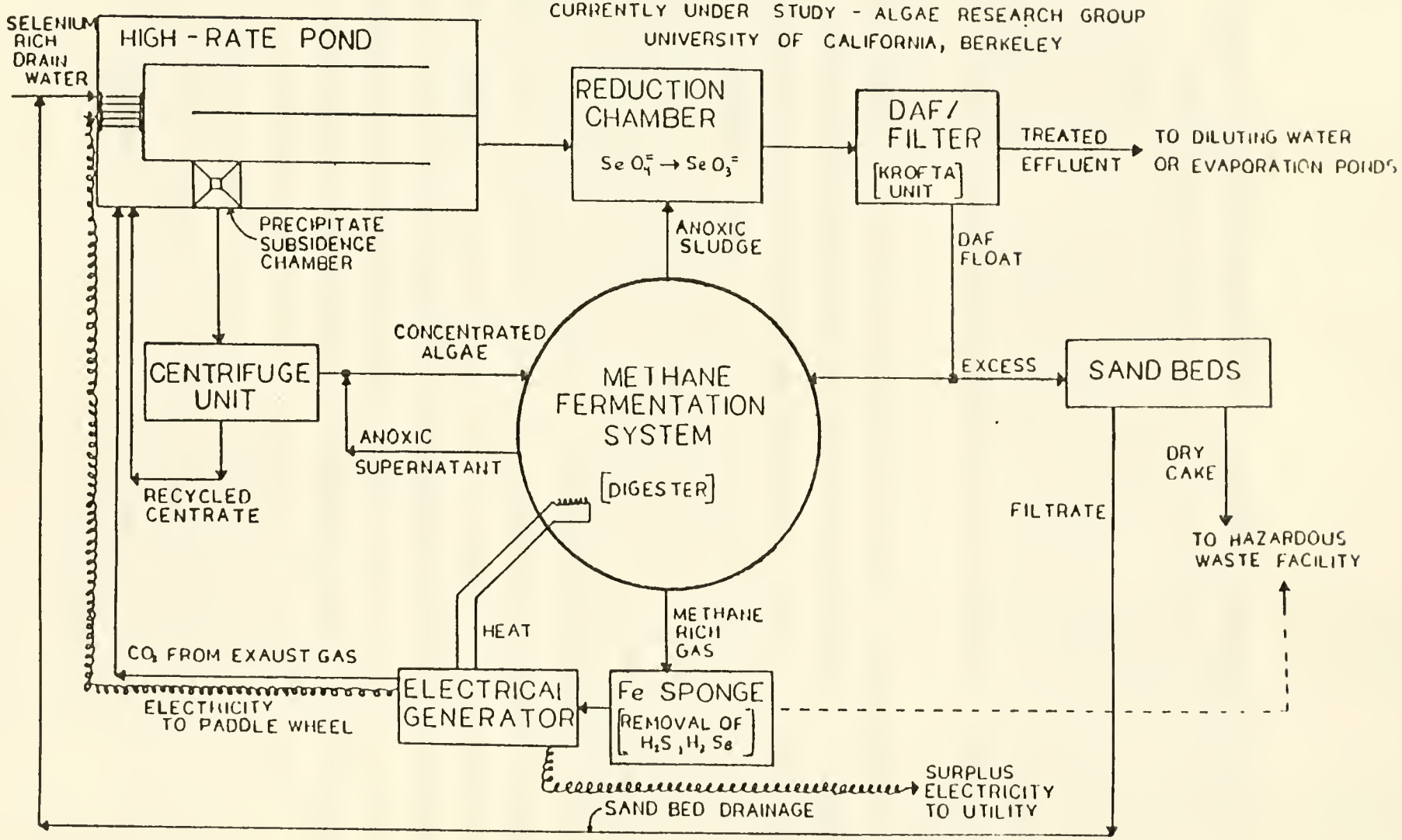
In this process, algae are produced in high-rate ponds (HRP) from the nutrient-rich drainage water to both incorporate nitrate in algal cells and provide biomass for methane fermentation. Sludges from the methane fermentation process have been observed to be effective reducing materials. The sludge would be introduced into a reduction chamber, where drainage water from the HRP will be in contact with the digested algal biomass. The selenium is expected to be reduced to an insoluble form and removable. Analytical work on a full bench-scale system is underway to evaluate the effectiveness of the concept. To minimize the size of the reactor, the soluble selenate must be converted as quickly as possible in the reducing chamber to insoluble forms. Also, there must be an adequate dependable supply of low-cost reducing material (sludge from the algal digesters).

Electrical power can be produced from the digester methane, which would operate the system with some possible energy surplus. Carbon dioxide from the power generation would be recycled to maintain a pH below 8.3 in the HRP and to provide carbon for microalgal growth. A schematic of the process is shown in figure I-2.

FIGURE I-2

SCHEMATIC DIAGRAM OF PROPOSED SELENIUM REMOVAL PLANT

CURRENTLY UNDER STUDY - ALGAE RESEARCH GROUP
UNIVERSITY OF CALIFORNIA, BERKELEY



A report on the concepts and initial laboratory studies was completed by Professor Oswald (1987) under funding from the SJVDP through the California DWR. Laboratory bench studies indicated that selenium in drainage water could be reduced from 90 to 99 percent with digested algal material.

A status report was prepared by Professor Oswald (1988) to update the progress of their work. He reported that prolific growths of algae was attained in drainage water at Murrieta Farms near Mendota, California. Harvested algae were effectively fermented in an anaerobic digestion system. The methane yield was 0.29 L/gm of volatile solids introduced in the digester. The methane fraction of the gas was over 70 percent, indicating a healthy methanogenic bacterial culture. The harvested algae was concentrated before digestion to reduce sulfate and nitrate levels in the digester feed, both of which can be unusually high at the Murrieta Farms drainage sump.

Digested drainage-grown algae reduced the soluble selenium concentration in the high rate pond effluent from 369 ug/L to 20 ug/L in the presence of ferrous chloride, achieving 95 percent removal of selenium. Some of the remaining (20 ug/L) may be colloidal selenium, which could be removed with better solids separation, such as a dissolved air flotation process envisaged in a full-scale system.

Further work remains on the duplication of laboratory successes for digestion and selenium removal under field conditions. Current laboratory work has been with batch reactors, and selenium removal in a continuous

flow unit has yet to be demonstrated. Currently, the SJVDP is funding further work on the microalgal bacterial process. An engineering assessment of the technology will be completed in late 1988, so that the process can be fully evaluated for technical effectiveness and cost economics.

Aerobic/facultative bacterial treatment. An "unsolicited proposal" of Dr. Richard Gersberg (1985) of the San Diego Region Water Reclamation Agency to use aerobic bacterial treatment was considered for SJVDP funding, but California DWR funded the proposal in 1986 to conduct initial studies on the process. The study results will be reviewed when they become available but further work has not been reported by Dr. Gersberg.

P. Altringer (1987) at the U.S. Bureau of Mines Research Center at Salt Lake City, Utah has been studying facultative bacteria in laboratory fixed-film static bed columns and in continuous flow rotating biological contactors, which were fed an organic food source. The bacteria used in these experiments were indicated to be Pseudomonas, Salmonella, and Citrobacter. Selenium was reduced from selenate to selenite and then precipitated in elemental form from solution. Selenium removal ranged from 87 to 96 percent. In one system, the selenium level was reduced from 3,800 ug/L to less than 150 ug/L in about 1 hour. Research is continuing at the Salt Lake City Research Center to improve reactor design, implement optional growth condition, and to understand the complex mechanisms involved in the process. A progress report is scheduled for late 1988.

In-situ biological processes. Two in-situ biological processes are under investigation for the management of toxic trace substances in the study area. The first study concerns the immobilization of selenium in soils and sediments as a means to attenuate or preclude its migration in ground-water systems. A research proposal for a study was submitted to the SJVDP in May 1985, after early discussions with Lawrence Berkeley Laboratory (LBL) staff of the University of California (UC), Berkeley. Continuation of discussions and an agreement for studies were completed with the USBR under its program for the cleanup and closure of the Kesterson Reservoir. Implementation of these laboratory and field studies were started in late 1985 and have continued to date. A series of progress reports have been issued on the investigation, including the 1987 annual report (LBL, 1987) and the latest progress report (LBL, 1988). A possible biogeochemistry for the immobilization of selenium in Kesterson Reservoir is shown in figure I-3. This is a simplification of a complex process, which is still under study. Nevertheless, key elements can be identified. Selenium appears to be immobilized in the sediment in organic, elemental, or metal forms. It is also gasified and emitted to the atmosphere. The water and sediment can have both aerobic and anaerobic phases, in which the process can naturally occur or can be stimulated. The selenium is adsorbed and held to the soil and sediment systems and thereby immobilized. The immobilization scheme is enhanced by keeping the sediment submerged and under high trophic conditions. The process probably occurs naturally, provided that the necessary environmental conditions exist. LBL scientists

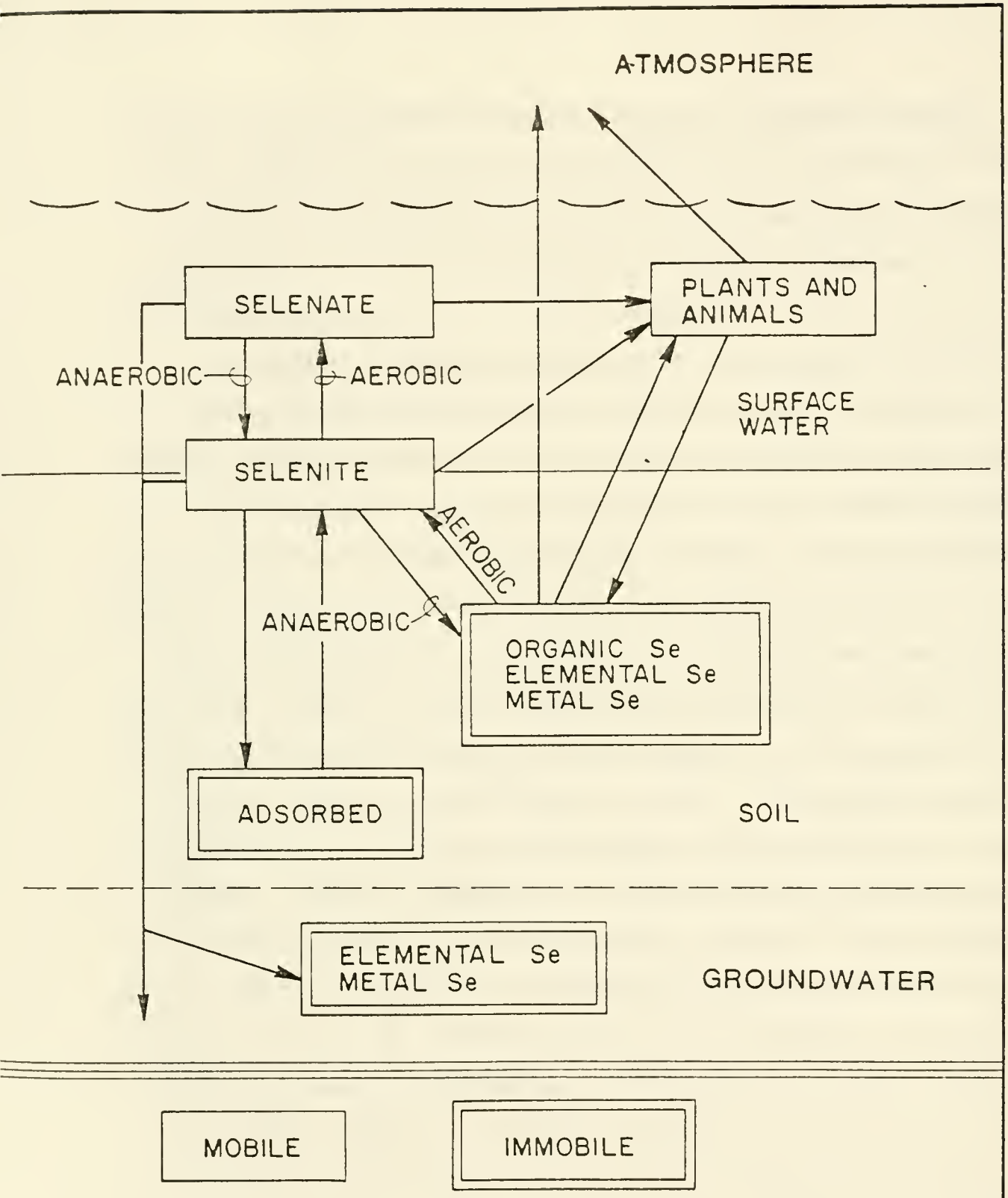


FIGURE I-3
POSSIBLE SELENIUM BIOGEOCHEMISTRY AT KESTERSON RESERVOIR
Source: USBR (1986).

reported that selenium has been largely contained in the upper sediments of Kesterson Reservoir and that ponds under study are showing much lower levels of dissolved selenium in the water column since the introduction of a new source of water. Selenium levels declined in surface water and in most of the primary food chain. These Kesterson Reservoir studies are still in progress to more fully understand the complex hydrological, geochemical, and ecological characteristics of biological immobilization of selenium.

The second in-situ biological process involves selenium volatilization. Professor William Frankenberger and Dr. Ulrich Karlson (1987) have been conducting research in their laboratory at UC, Riverside, on microbial methylation of selenium and have produced results indicating that a natural process of volatilization can be significantly accelerated. Their initial studies were funded by the UC Salinity/Drainage Task Force. A schematic of the Frankenberger-Karlson Process is shown in figure I-4. SJVDP staff discussed in April 1987 with Professor Frankenberger the possibility for the application of this process to the study program. A research proposal was submitted subsequently to the SJVDP for evaluation and funding support. Since then, the research on volatilization from soils has been incorporated into studies funded by the USBR's Kesterson Reservoir cleanup program, where a more urgent problem exists.

A progress report on the Kesterson Reservoir study was prepared by Frankenberger (1988). Findings to date provide support to potential application of the process for the detoxification of seleniferous soils.

The Frankenberger-Karlson Process

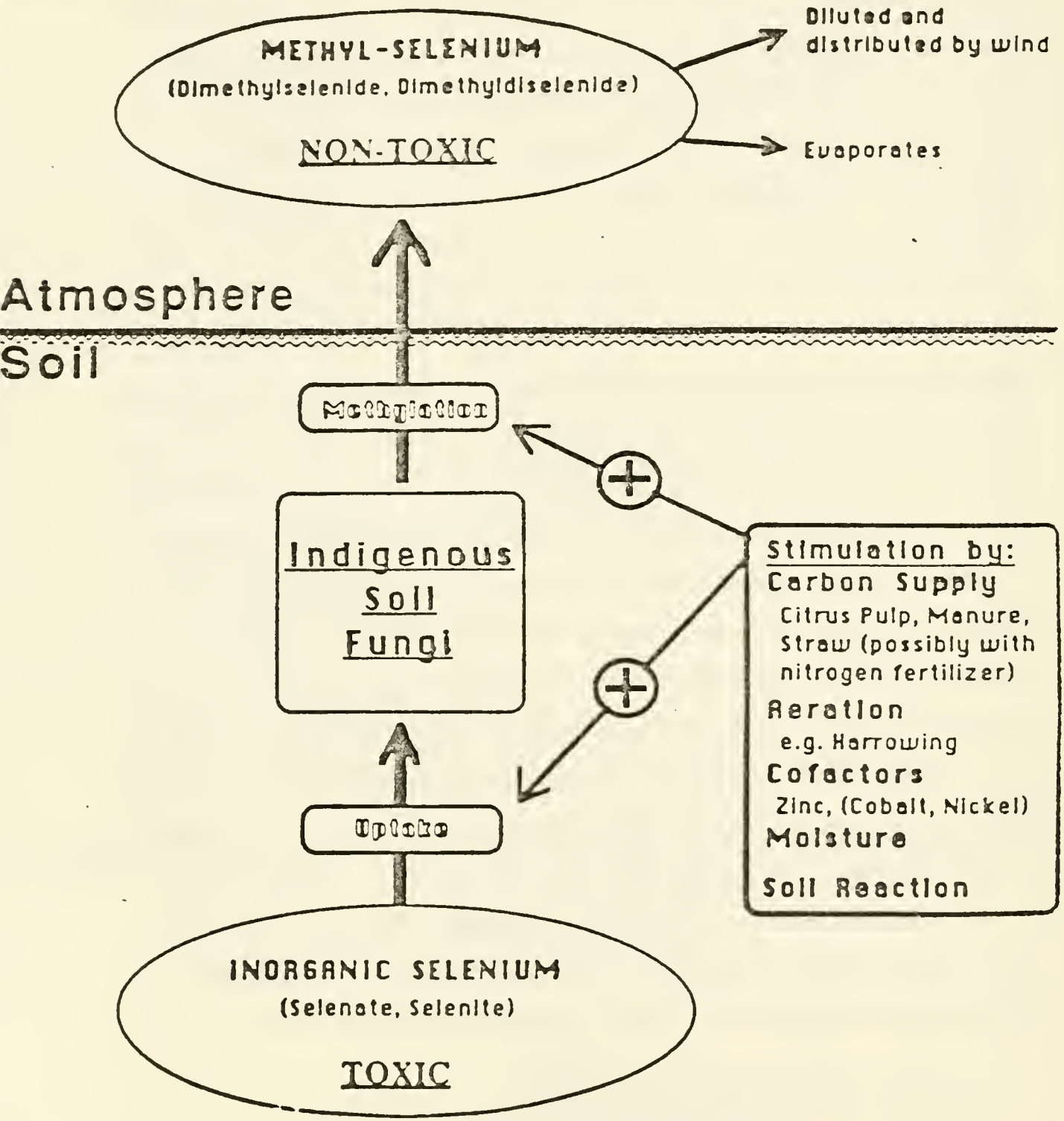


Figure I-4. The Frankenberger-Karlson Process.
Source: Frankenberger (1987).

In the laboratory, it was shown that fungi could take up selenium salts and biologically convert them into methylated species, primarily dimethylselenide and dimethyldiselenide. Methylated gas forms are naturally volatilized into the atmosphere and dispersed.

The process is biologically stimulated by carbon sources, moisture, aeration, and activators. Zinc, nickel, and cobalt appear to be good activators, as well as nitrogen additives. Adequate aeration and moisture are needed to sustain the obligate aerobic fungi.

Field studies were initiated in July 1987 at Kesterson Reservoir. Citrus pulp, cattle manure, and straw were used as carbon sources and ammonium nitrate, ammonium sulfate, and zinc sulfate were added to some test plots. The upper layers of the soil were kept moist to maintain the process.

Monitoring of field level selenium volatilization was made with a dome capture device. Emission rates were measured from October 1987 to February 1988. The highest rate of emission of methylated selenium was recorded in October at 363 ug/m^2/hour. Citrus pulp enhanced volatilization to the best level, compared to other organic sources. Temperature and moisture levels greatly influenced the process. Diurnal and seasonal temperatures are important factors on the emission rate.

Selenium removal by volatilization was reported to be as high as 50 percent in a 4-month period, in controlled laboratory conditions. Studies indicate that there is no minimal threshold limit and, therefore, the process can potentially reduce selenium to very low levels. The

toxicity of methylated selenium gas forms is under study at the University of California at Davis, to evaluate any health problems associated with releases to the environment.

Studies on sediments of evaporation ponds which have been dewatered, are also under way, as a detoxification process using the Frankenberger-Karlson Process. These studies at the Peck Farm ponds at Fresno County are under funding support of the State Water Resources Control Board, the Westlands Water District, and local agricultural interests.

Anticipating that evaporation ponds in the San Joaquin Valley could be hazardous to the environment, and some may eventually violate hazardous waste containment criteria (especially for selenium), the SJVDP also funded studies by Professor Frankenberger on the volatilization of selenium from evaporation ponds. The work is intended to increase the rate of microbial volatilization from stored drainage water. The researchers will field test the process at an evaporation pond site in the valley.

Enhancement of microbial methylation of arsenic, mercury, and tellurium may also be possible. Frankenberger (1987) submitted to SJVDP a proposal to conduct a literature review to assess the potential to enhance volatilization of these elements, but this proposal has been held in abeyance for possible future funding support.

Studies to date indicate that in-situ treatment by microbial methylation of contaminated water and soil systems may have promise for development into a feasible approach. An integrated approach involving microbial immobilization, followed by volatilization processes, may be able

to decontaminate soil and water systems. At this time studies are under way only on separate systems to understand better the individual processes for possible application to field level decontamination.

Chemical Treatment

Ferrous hydroxide. The USBR's Denver Office has conducted laboratory bench and batch reactor studies, funded by the SJVDP, using ferrous hydroxides to reduce and precipitate selenium from drainage water (see figure I-5 for schematic). A paper was presented on the theoretical aspects of ferrous hydroxide reduction of selenate by Murphy (1988). Moody, et al. (1988) published a status report of the batch reactor studies conducted in the laboratory and at Murrieta Farms, Mendota. Studies thus far lead USBR researchers to conclude that selenate can be chemically reduced to elemental selenium and removed from drainage water using ferrous hydroxide treatment. Data show no sulfate interference, so the process may be applicable to the selective removal of selenate in high sulfate waters. The reaction has been observed to occur between selenate and ferrous hydroxide under alkaline conditions producing iron oxides and elemental selenium. Laboratory reaction rates with varying dosages of ferrous hydroxide are shown are figure I-6. The laboratory reaction reduced selenate down to less than 5 ug/L within one minute. However field studies at Murrieta Farms indicated slower rates (see figure I-7). In the best run (test 3), selenate was reduced by about 90 percent in 2 hours but reduction to higher levels took up to 6 hours.

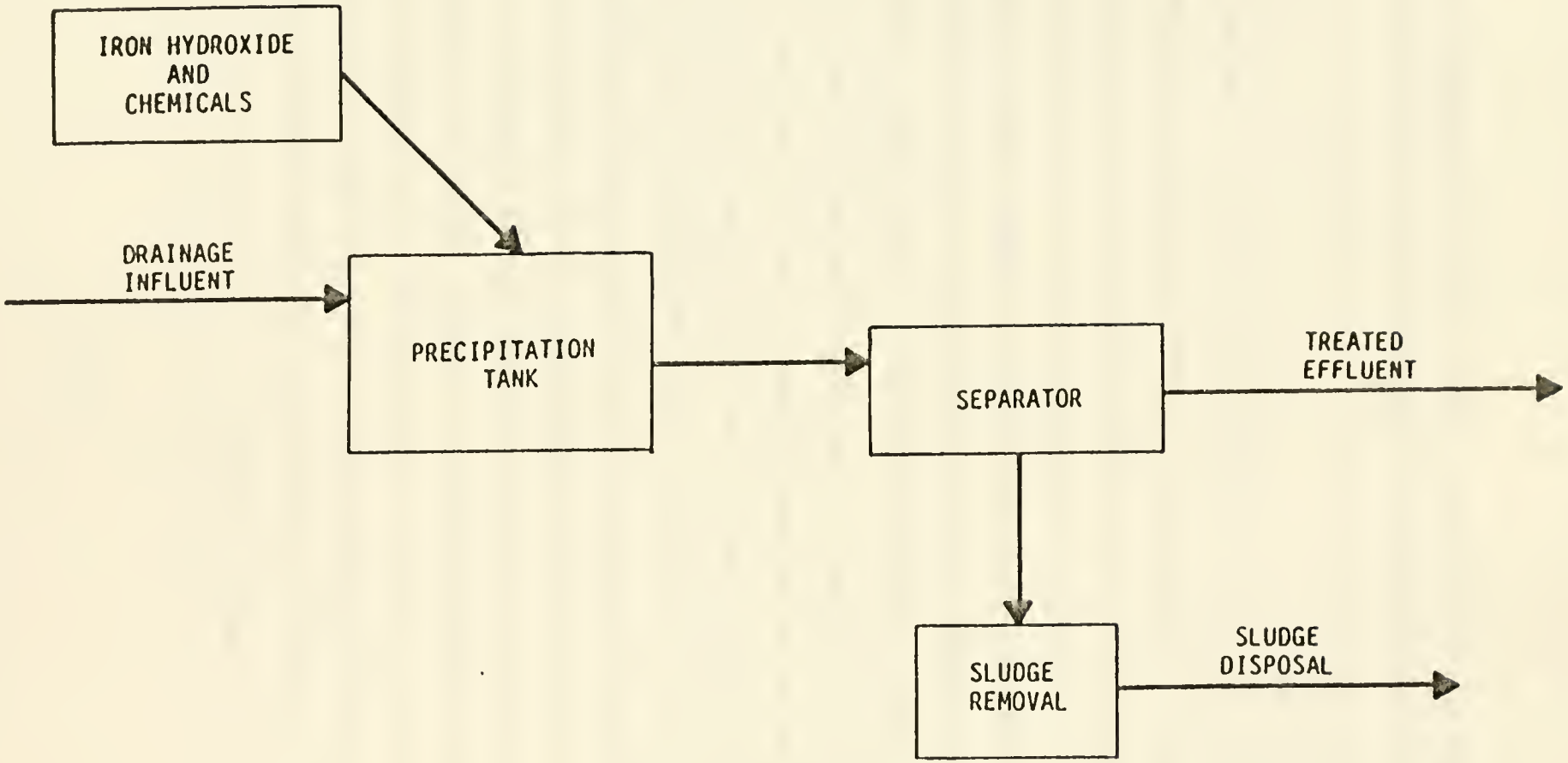


Figure I-5. Iron hydroxide treatment selenium removal plant schematic.

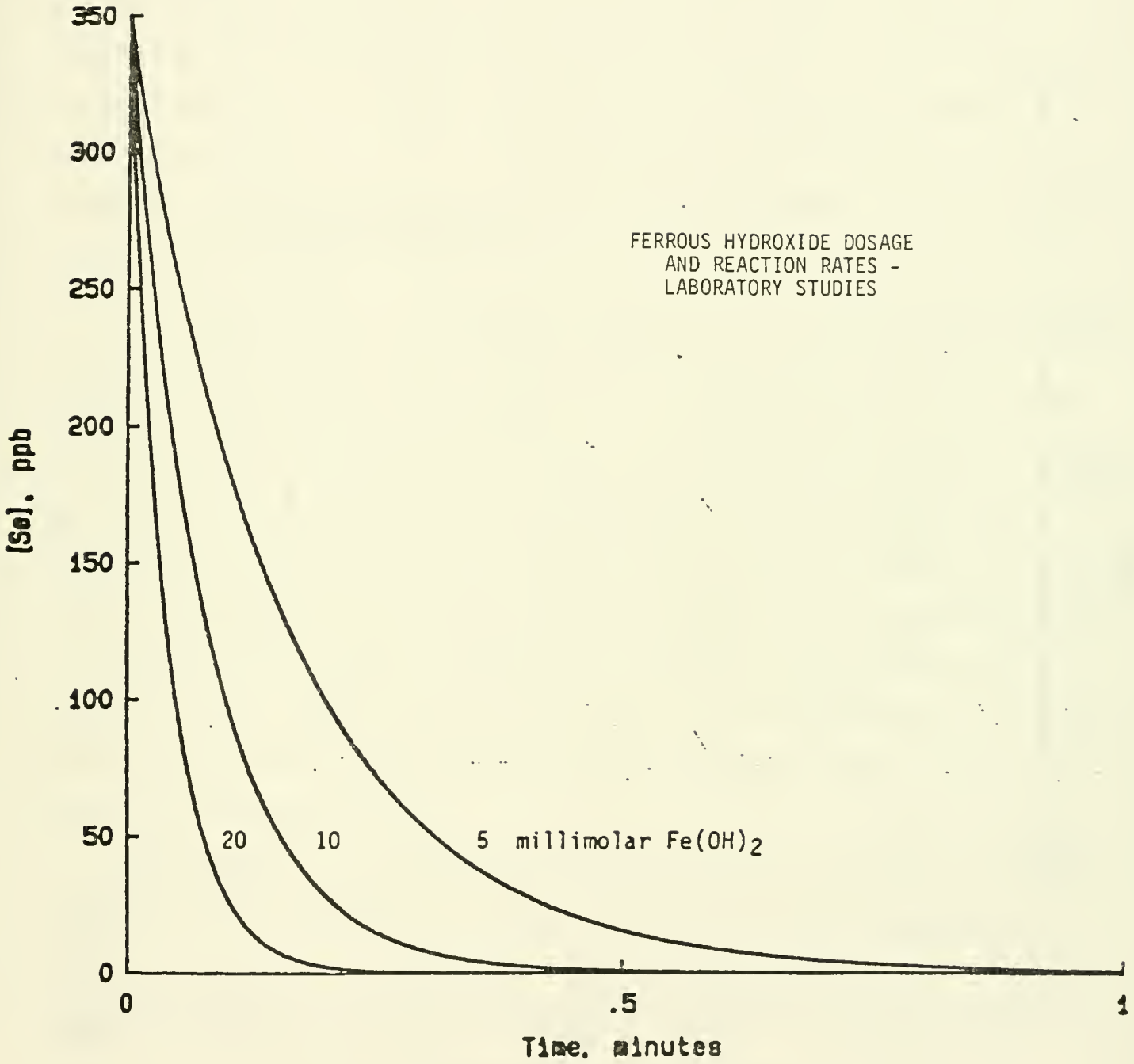


Figure I-6. Ferrous Hydroxide treatment.
Source: Engineering & Research Center, USBR (1988)

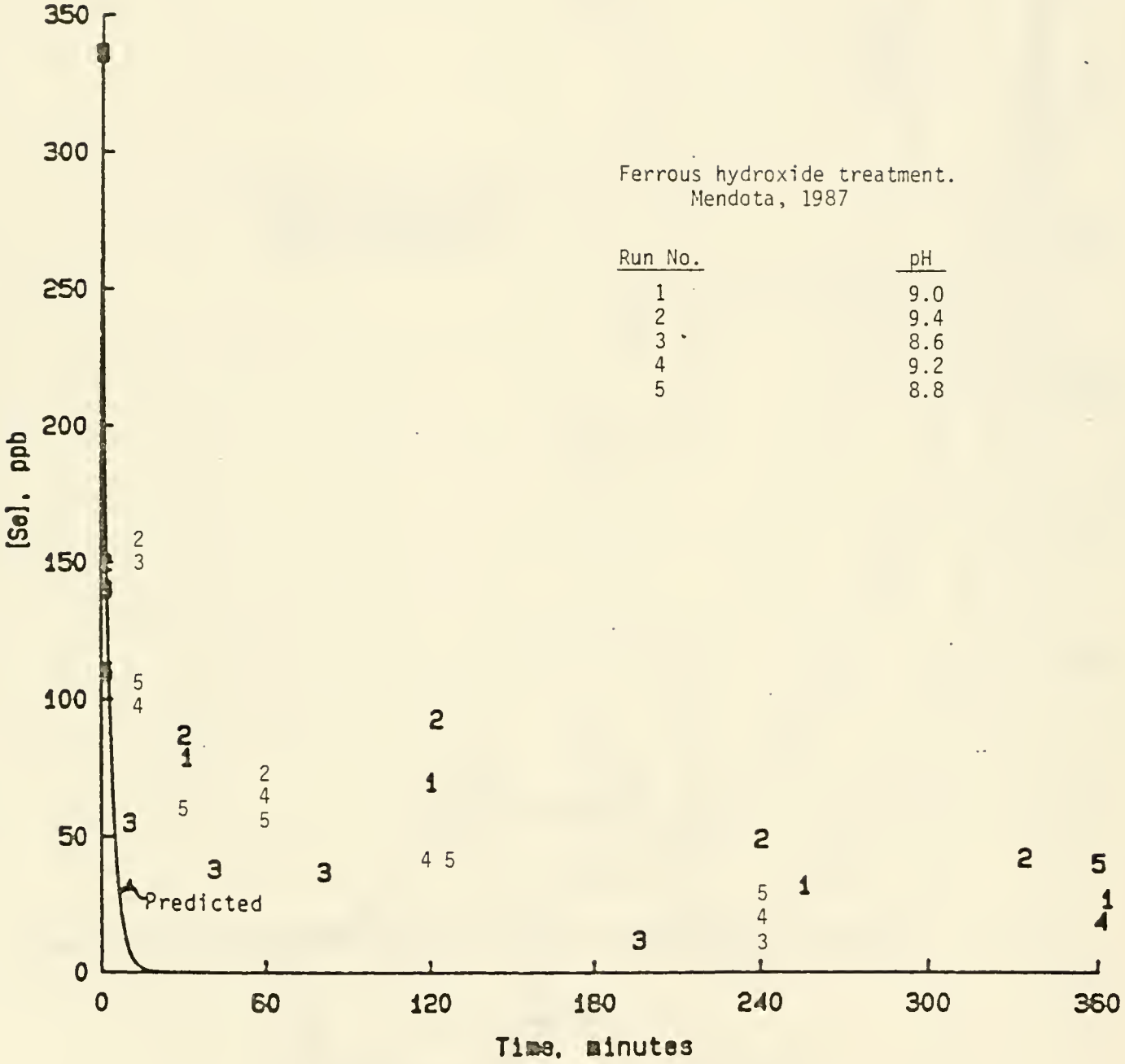


Figure I-7. Ferrous hydroxide treatment.
Source: Engineering & Research Center, USBR (1988).

Preliminary consideration of plant design includes stirred reactors, followed by gravity settlers, in several flow configurations. A major cost of the treatment process would be for the ferrous hydroxide. This chemical can be made from ferrous sulfate and sodium hydroxide and can be expensive, depending on dosages required. An alternate and less costly method to produce ferrous hydroxide is to use calcium oxide and ferrous sulfate and this is under study.

The chemical dosage appears to be determined mainly by the dissolved oxygen level in drainage water. Water quality monitoring of field drains indicate a wide variability in oxygen levels. It appears that dissolved oxygen must be diminished before selenate can be converted to insoluble forms by the ferrous hydroxide. Other constituents including nitrates may also interfere with the process and studies are in progress to identify them. The process can also reduce other trace elements at the same time. Current plans are to complete assessment of the process by mid-1988 and to decide on future studies, which could include a pilot prototype plant to gather detailed data and information on cost, effectiveness, and operational characteristics.

Other chemicals. Various other chemicals have been suggested for the reduction and precipitation of selenate. The Denver Office, USBR, was assigned to screen and to evaluate the more promising chemicals. A draft report was submitted by Price and Eisenhauer (1988), covering the screening of chemicals for possible development into process trains. The report on their laboratory screening tests of the following compounds concluded:

- o Thiourea and sulfuric acid removed about 66 percent of the selenate.
- o Thiourea, sulfuric acid and sulfur dioxide removed about 91 percent.
- o Insoluble starch xanthate (ISX) removed about 15 percent of the selenate.
- o Iron sulfide (powdered iron pyrite) removed about 24 percent of the selenate.
- o Sodium thiosulfate removed about 10 percent of the selenate.
- o Insoluble sulfide precipitation process (sulfex process) did not remove any selenate.
- o Soluble sulfide precipitation process did not remove any selenate.
- o Hydrazine sulfate (sodium tri-thio-carbonate, X-154 compound of Iso-Clear Systems Corp.) did not remove any selenium.
- o CYC Compound (Iso-Clear Systems Corp.) removed about 8 percent of the selenate.

The report recommended further studies be conducted to optimize removal processed with: (1) Thiourea, sulfuric acid, and sulfur dioxide, (2) iron sulfide, and (3) sodium thiosulfate. These recommendations are currently under evaluation for possible future funding support.

In-situ physical/chemical attenuation. Professor Gary Sposito and Dr. Rosemary Neal of the University of California, Riverside, are studying selenite and selenate attenuation, or lessening, of San Joaquin Valley soils in experimental soil columns. If successful, the batch studies will

be extended to field studies in the San Joaquin Valley as a means for in-situ management of selenium. Professor Sposito's batch studies, like Professor Frankenberger's earlier microbial methylation studies, were funded by the UC, Salinity/Drainage Task Force. The present project, funded under the SJVDP, is a phased study examining selenium movement in laboratory soil columns maintained under simulated drainage regimes similar to those in the valley.

Professor Sposito commenced work in September 1987 and has thus far completed design of the column test system and has developed an improved technique for the determination of selenate and selenite in aqueous solution. Literature and current unpublished research have also been reviewed on the state of knowledge about the speciation of selenium in field soil profiles. To identify the best manipulation of chemical characteristics of soils to maximize selenium attenuation, the behavior of selenium, and, in particular, selenate, in the soil profile must be understood. In the second stage of the project, experiments will be conducted to study the fate of selenate in irrigation and drainage water as a function of time, pH, and redox conditions, when tested in a series of soil columns.

Physical Adsorption

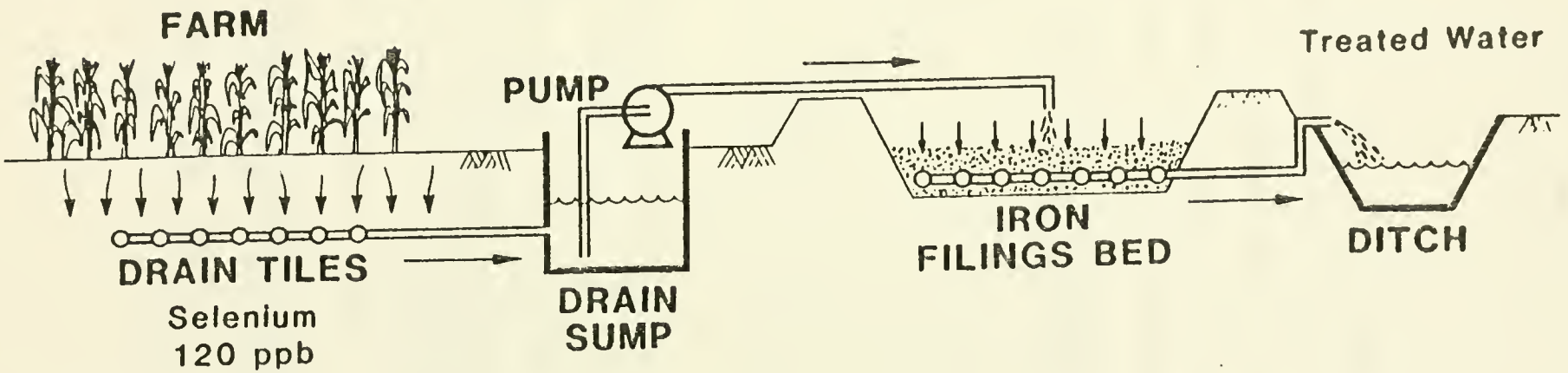
Iron filings. Harza Engineering Company conducted field studies with iron filings as an adsorption material in a minipilot plant at the Panoche Drainage District in 1985 and published a report (Harza, 1986). They used a process patented by Mayenkar (1986) of Harza, which is based on the

physical adsorption of heavy metals on iron filings. A schematic of their process is shown in figure I-8. It was claimed that the surface of the iron filings could be activated by oxygenation and that selenium was adsorbed on the activated surface.

A major problem encountered in the columns used in the studies was the cementation of the iron filings. The cause for the plugging of the columns was not explained but possibly could be due to the precipitation or the coagulation or occlusion of drainwater constituents. This can have impacts on the bed life, treatment effectiveness, and cost affordability. Preliminary studies indicated that a wide range of costs can be expected, depending on bed life and removal expectancies (see figure I-9). From available test data, a reactor time of 2 hours is required for 50 percent removal and 4 hours for 75 percent removal. With a 5-year adsorbent bed life, the estimated cost is about $70/acre-ft for 50 percent removal and $120/acre-ft for 75 percent removal. However, if bed life were to be reduced to 2 years, the cost would increase to $160/acre-ft (50 percent removal) and $285/acre-ft (75 percent removal).

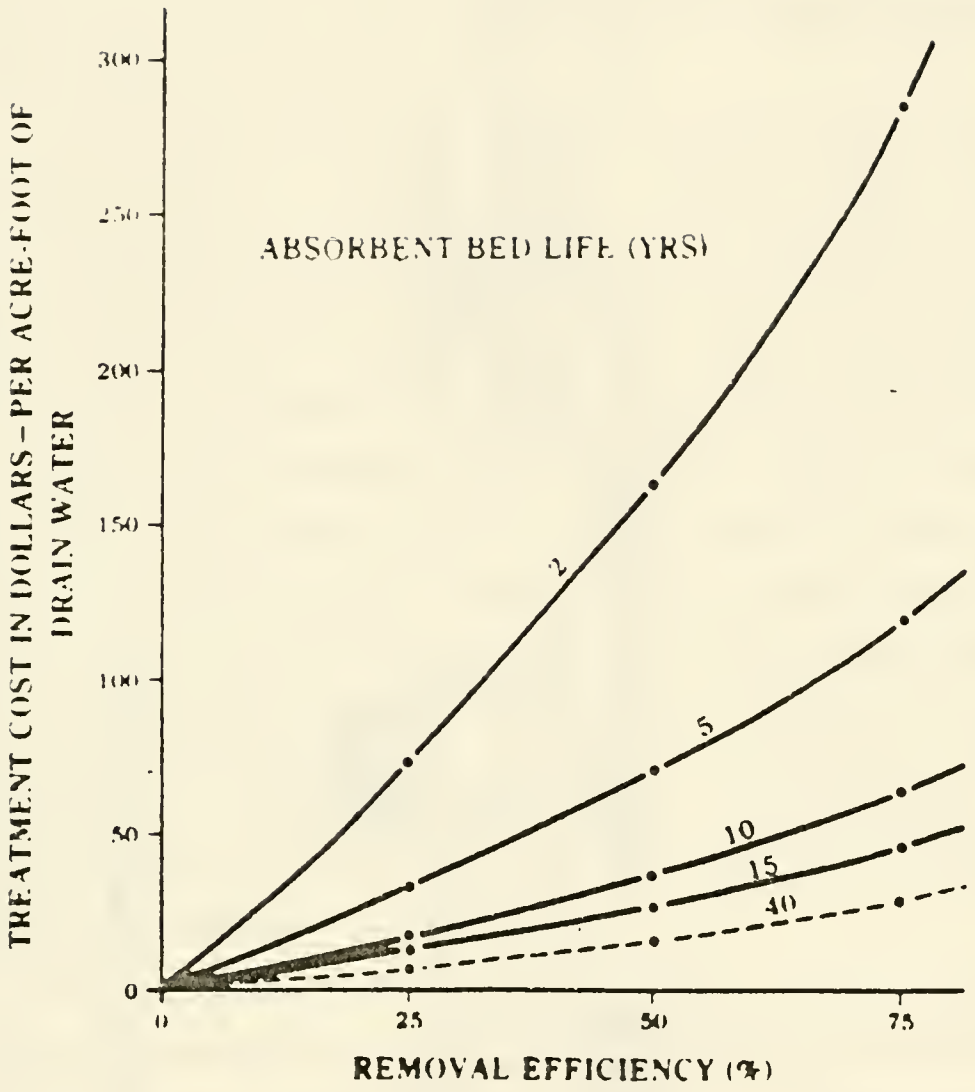
A pilot prototype plant has been under design for installation and operation in mid-1988 at the Panoche Drainage District to gather detailed technical and cost information to determine the engineering feasibility of the process, including better estimates of bed life.

Ion exchange resins. Dr. C. Hermann (1985) of UC Berkeley completed a literature review for the SJVDP on the use of ion exchange resins and



A Schematic Diagram of On-farm Selenium Removal Plant

Figure I-8. Schematic diagram of of-farm selenium removal plant.
Source: Harza Engineering Corporation (1986).



Treatment Cost by Removal Efficiency for different bed lives

Figure I-9. Treatment cost by removal efficiency for different iron filing bed lives.
Source: Harza Engineering Corporation (1986).

concluded that, because of the complex chemical composition of agricultural drainage water, an ion-specific resin would need to be developed.

The SJVDP funded a study in 1987 by the Boyle Engineering Corporation (Boyle), to demonstrate selectivity of specific resins for ion exchange treatment of drainage water using selected commercially available resins.

Ion exchange treatment for removal of selenium from valley agricultural drainage water is very difficult because of the extremely high concentration of sulfate and chloride ions relative to selenium. Boyle is studying selenium-selective resins that would preferentially remove selenium in the presence of high sulfate and chloride concentrations. Bench-scale column tests of the process have been conducted with drainage water samples.

Dr. J. Guter of Boyle reported (1988) from their studies that two strong-base anion resins, both similar to commercial type resins, but having larger alkyl groups in place of the trimethyl, showed selectivity for selenate ion over sulfate ion. Guter believes that the selenate to sulfate selectivity appears to be directly related to the size of the alkyl groups in the resin, and this potential can be enhanced. The SJVDP is reviewing Boyle's report and the results of its work thus far, in weighing future development in ion exchange treatment with selective resins.

Electrochemical Treatment

Electrocoagulation. This process entails applying a direct current through a reactor cell containing alloy steel electrodes. Ferrous ions which would form would reduce and precipitate heavy metals. The process is reported to have been tested at laboratory and field scales by Duffy (1985) of ANDCO Environmental Process. It is reported that on a single pass through the reactor, about 50 percent of the selenium was removed. Preliminary estimates indicate that this would be an expensive process, since achieving a higher level of removal this would require multiple passes through the system. Further work has been kept in abeyance.

Electron exchange resins. The Denver Office of the USBR conducted laboratory tests of an electron-exchange resin and found that selenium was being removed. The USBR initially used an old stock of resins, which was depleted. When a new stock of the resin was obtained from the same manufacturer, the USBR was not able to duplicate the earlier results. The staff concluded that the mechanism was not an electron-exchange process, but rather an ion-exchange process. A report is under preparation by Price and Eisenhauer (1988) on these findings, with a recommendation that further studies should not be pursued with electron-exchange resins.

Desalination

The desalination of drainage water provides an attractive option to reduce salinity (TDS), as well as trace elements. Moreover, the possibility exists for the recovery of usable water for agricultural, industrial, or municipal uses. The SJVDP reviewed many desalination

processes and this review, based largely on the work of Toups (1982) has been summarized in Appendix B, as background information. Most processes are considered energy intensive and costly for agricultural drainage water. Many wastewater treatment experts believe that the most applicable process for desalting drainage water would be the use of reverse osmosis (RO) membranes and accordingly this technology was evaluated.

Reverse osmosis. This section reports on the study by the consultant CH2M Hill (1986), for the SJVDP, to evaluate the potential for the use of RO in the treatment of drainage water. Although the results of this study are the principal subject of the ensuing discussion, results from the USBR's Yuma and DWR's Los Banos desalting facilities are also discussed, to report from a broader base of experience in reverse osmosis technology for drainage treatment.

Pretreatment is critical to successful RO operation, and it was a key part of the CH2M Hill study. Three pretreatment schemes were studied (see figure I-10 for schematic illustrations). The CH2M Hill Study was a conceptual-level study for a 10 Mgal/d RO desalting plant to treat water from the San Luis Drain. It was directed that the study be based on treatment processes that are considered proven, off-the-shelf technology. The exception was that the relatively untested brine recycle pretreatment process was also to be thoroughly studied to evaluate the current state of the art on this specific subject. The brine recycle process is in its developmental stage. It was tested by the USBR at the Verkin Springs,

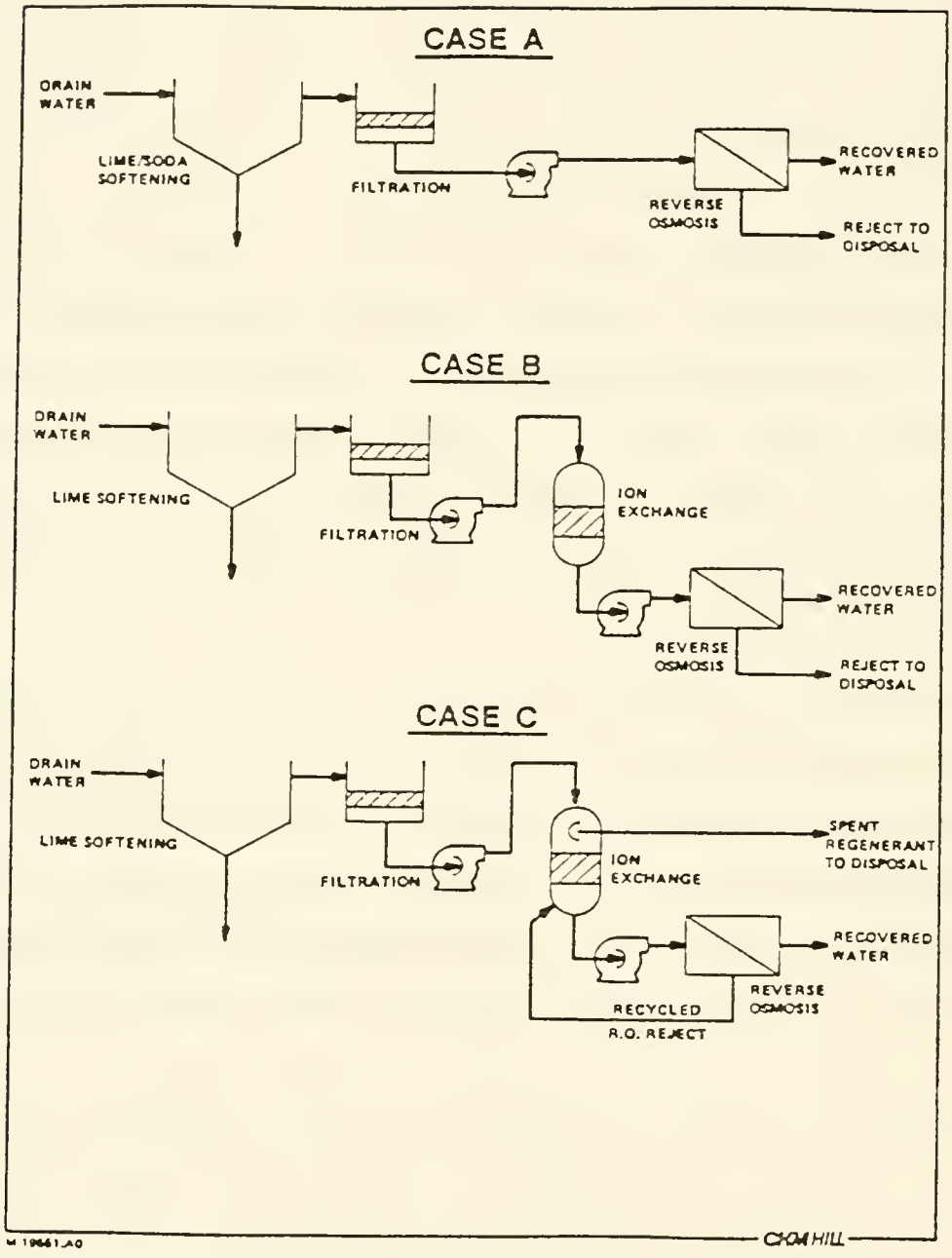


Figure I-10. Desalting alternatives.

Utah, and is under investigation by DWR at Los Banos, California. It has not been implemented at project level application.

In all cases pretreatment included multimedia filtration, chlorination, and dechlorination. CH2M Hill reported that the pretreatment would not remove selenium, which is almost entirely in the selenate form, or boron but would remove most of the other trace metals. All of the pretreatment approaches were expected to be capable of achieving a maximum of 87.5 percent RO recovery.

Lime/soda ash softening (Case A) is a commercially proven process that has been in use for over 50 years. It uses lime and soda ash to reduce carbonate and noncarbonate (calcium and magnesium) hardness. Noncarbonate hardness is not affected by lime alone, so soda ash must be added. Because of the low carbonate hardness of the San Luis Drain water, a large amount of soda ash is required. CH2M Hill reported that calcium removal is critical because the RO unit requires a calcium effluent with a softness of less than 75 mg/L as $CaCO_3$ to achieve 87.5 percent recovery.

The ion exchange process (Case B) uses strong acid resin and exchanges calcium and magnesium for sodium. It was reported that this process would remove the divalent and trivalent trace metals but at an unknown efficiency. Boron and selenium would not be removed since they would be in the anion form.

The capacity of the resin, or the volume of water treated per unit volume of resin, is influenced most by:

- o The quality of the feedwater (relative concentration of sodium, calcium, and magnesium).
- o The amount of salt used in regeneration.

The resin is regenerated when its capacity is exceeded, and unacceptable levels of calcium and magnesium remain in solution after ion exchange. To regenerate the resin, a sodium-chloride solution (NaCl) is passed through the resin bed, reversing the exchange reaction. The regenerant is conventionally a fresh NaCl solution or the RO reject brine, as was being tested by the California Department Water Resources at its Los Banos facilities. CH2M Hill estimated about 220 tons per day of NaCl would be required for brine regeneration.

The principal advantage of the recycled brine regeneration process (Case C) is the significant savings in reducing the use of fresh NaCl for regeneration. However, the amount of sodium available for regeneration from the RO brine is limited to the sum of the sodium in the feedwater and the sodium exchanged from the resin for hardness removal. Two reported potential hazards of using RO brine for regeneration are: (1) The amount of regenerant available is limited to the salt available in the reject brine solution, and (2) the brine contains significant amounts of calcium sulfate ($CaSO_4$), a low solubility salt.

At La Verkin Springs, the results of resin regeneration using desalting process brine was comparable to conventional salt regeneration. However, a brine equivalent of 60 pounds of NaCl per cubic foot of resin

was needed to achieve the same ion exchange capacity as with 20 pounds of NaCl using conventional salt regeneration. Larger salt dosages were required because of the lower sodium concentration in the desalting brine.

As recovery increases in RO systems, more concentrated RO brines, which are more effective for regeneration, are produced. On the other hand, as RO recovery increases, the calcium and sulfate levels increase, more closely approaching calcium sulfate saturation.

For all of the pretreatment in the above cases CH2M Hill included chlorination to inhibit biological growth, which can shorten membrane life and foul the filter media. Multimedia filtration was also included to remove suspended and colloidal matter before the RO process. These matters can cause fouling and premature failure of the RO membranes.

The RO process studied by CH2M Hill was based on a three-stage system, the first operating at 400 to 450 lb/in^2, and the second and third stages operating at 850 to 900 lb/in^2. A simplified schematic diagram of the process is shown in figure I-11. The membranes were spiral wound polyamide thin-film composite. With effective pretreatment, the RO unit was expected to operate at an average of 83 to 87 percent recovery. The product water would have a TDS concentration of 550 to 650 mg/L, while the brine would have a TDS concentration of 55,000 to 67,000 mg/L. Excluding selenium, the trace metal levels were expected to be below detection levels by conventional analytical methods. The selenium concentration would be about 10 to 20 ug/L. Boron would be only partially removed; 7 to 8 mg/L would remain in the product water (San Luis Drain water averaged about 14 mg/L).

REVERSE OSMOSIS DESALTING

From Study by CH2MHill for San Joaquin Valley Drainage Program

Simplified Schematic Diagram

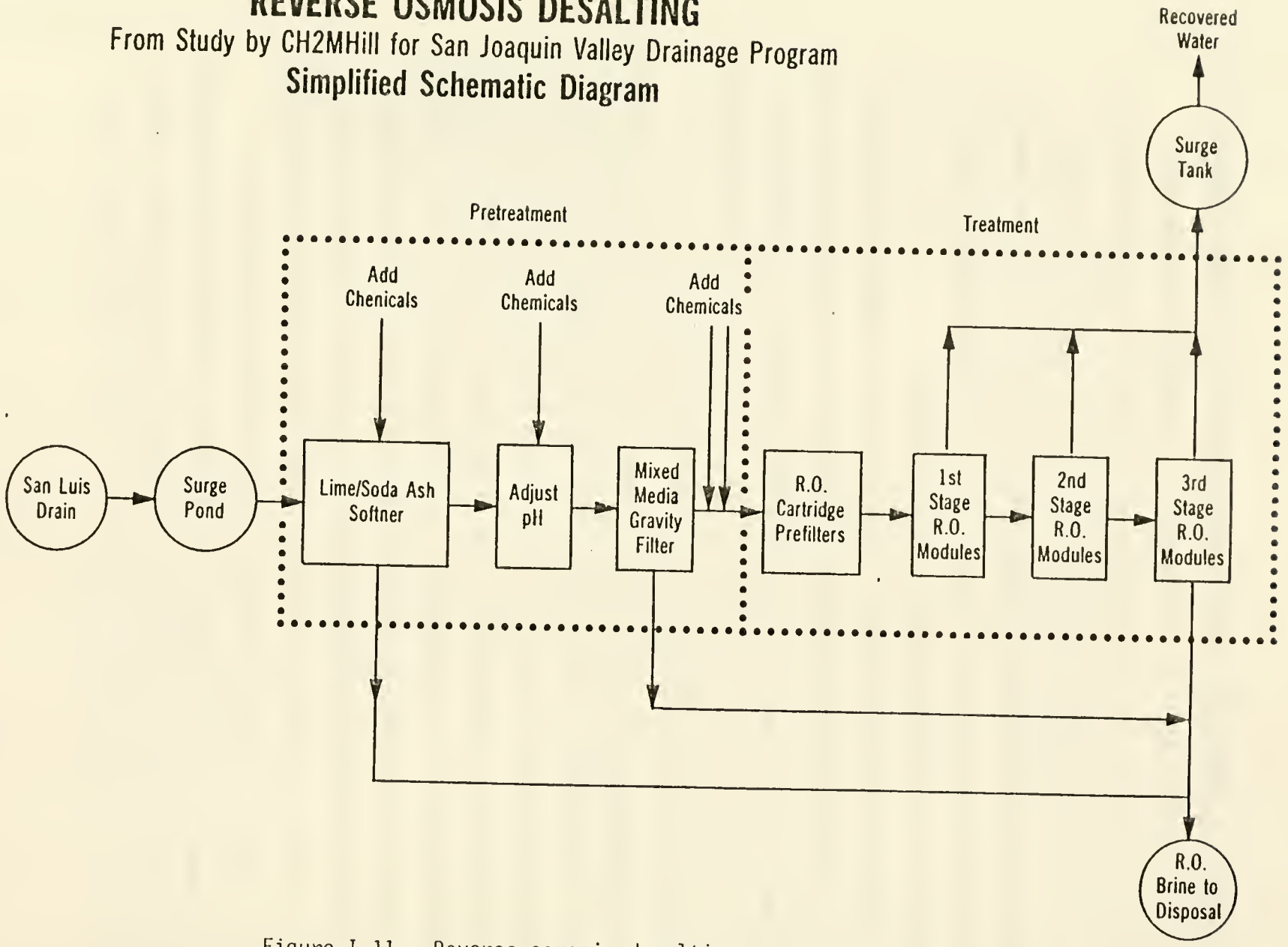


Figure I-11. Reverse osmosis desalting.

CH2M Hill considers 87.5 percent reverse osmosis recovery high for commercial installations, especially for the high TDS level in the feedwater. Also, the third stage membrane life would probably be less than normal. Nevertheless, they used 87.5 percent as the design recovery target (despite approaching the probable upper limit for calcium scale free operation) because:

- Ion exchange regeneration with RO brine (Case C) is easier with higher-strength brine,
- Costs for waste brine evaporation ponds rapidly increase inversely to RO recovery; and
- Ongoing improvements in RO equipment and RO application technology may improve high recovery operation.

CH2M Hill reports that disposal costs increase rapidly with lower recoveries. It cited, for example, that the wastewater generated at 75 percent recovery is twice the rate generated at 87.5 percent recovery.

At construction costs of up to about $200,000 per acre for toxic waste ponds in California (Class I), disposal cost is a major consideration in evaluating desalting systems. This is a relevant point because, after the release of the CH2M Hill report by the SJVDP, the validity of the CH2M Hill cost estimates was questioned--largely because of the high RO recovery on which the report was based. It has been suggested that 50 percent, rather than 87.5 percent, recovery should have been used. There is merit to lowering the recovery rate for the sake of the RO system efficacy, but the CH2M Hill cost estimate is still basically sound. Lowering the recovery

rate to 50 percent will lower the costs of pretreatment and RO, but will also produce an offsetting (not necessarily equal) disposal cost in the very expensive Class I ponds.

Brine disposal is also a major consideration in desalting systems. CH2M Hill determined that an evaporation/disposal pond must dispose of the entire reject brine stream. The results were as follows:

	Waste Stream (Kgal/day)	Number of Evaporation Cells (40 acres each)	Evaporation Area (acres)
Case A	1,326	7	280
Case B	2,512	13	520
Case C	1,865	10	400

Cases A, B, and C generate 113,000, 165,000, and 109,000 tons of salt per year, respectively. The pond acreages were determined on the basis of holding 6-foot-deep salt and water mixtures in each cell after 20 years of service. Near the end of the 20-year service life, the ponds would be nearly filled with accumulated salts.

The cost of ponds will be a significant part of RO treatment cost. If California Class II ponds for designated wastes are acceptable, CH2M Hill estimates that the cost of ponds would amount to about $10 million, but the cost would increase to about $104 million if Class I ponds are required. In view of the selenium level exceeding 1 mg/L in all of the three cases, Class I ponds would likely be required for in-valley disposal of brines.

Cost for RO is a very important consideration in evaluating desalting as a solution of the drainage problem, although desalting provides the widest options for the reuse of drainage water. Desalting of drainage

water will be expensive. CH2M Hill estimated in its study that it would cost $1,090/acre-foot of raw water treated under Case A, CH2M Hill's recommended process table I-4. If the wastestream could be disposed in Class II ponds, the cost increases to $1,140/acre-foot. More realistically, however, Class I ponds would be required, in which case the cost would further increase to $1,650/acre-foot.

Sensitivity analyses were requested of CH2M Hill to show the effects of interest rates, energy costs, and RO recovery rates on RO treatment costs. The effects are illustrated in figure I-12 for Case A, the recommended process.

CH2M Hill was directed to base its cost estimates on a 6 percent interest rate and a $.075/kWh energy cost, as were other contract consultants in the evaluation of drainage solution options. Figure I-12 shows that unit costs using Class I ponds increase rapidly with increasing interest rates, while costs for Class II ponds are less sensitive. This is because of the high capital cost of construction of Class I ponds. CH2M Hill estimated the cost of Class I ponds to be about $200,000/acre and $20,000/acre for Class II ponds.

Energy cost has a significant bearing on the unit cost of RO desalting because the process has a significant energy demand. For comparison, CH2M Hill was asked to look into costs using an energy rate of $.0067/kWh, the USBR energy rate for the Central Valley Project (CVP). The unit cost difference between energy costs of $.075/kWh (commercial rates) and

Table I-4. Cost Summary 10 Mgal/d Desalting Facility
San Luis Drain at Mendota[f]

	CASE A	CASE B	CASE C
Pretreatment Method	Lime/Soda Ash Acid Scale Inhib.	Lime Ion Exchange (conv. regen.) Acid Scale Inhib.	Lime Ion Exchange (recycle regen.) Acid Scale Inhib.
Raw Water Feed (AF/Yr)	8,700	8,700	8,700
Treated Water Recovery (Acre Feet/Yr)	7,600	6,500	7,000
Treated Water Quality[a]			
TDS (p/m)	640	570	560
Selenium (p/b)[b]	-3	-3	-3
Boron (p/b)	7,600	7,600	7,600
Capital Investment[c]	$21,200,000	$27,200,000	$28,100,000
* * * * * * *			
Capital Charge ($/Kgal)[d]	0.65	0.85	0.85
Operating Cost ($/Kgal)[e,g]	2.70	2.90	.15
COST FOR DESALTING			
($/Kgal raw water)	3.35	3.37	3.00
($/acre-foot)	1,090	1,220	980
COST INCLUDING CLASS II WASTE PONDS ($/Kgal)	3.50	4.05	3.25
($/acre-foot)	1,140	1,320	1,060
COST INCLUDING CLASS I WASTE PONDS ($/Kgal)	5.05	6.90	5.45
($/acre-foot)	1,650	2,250	1,780

[a]Influent water quality: TDS = 9,820 p/m
Se = 325 p/b
B = 14,400 p/b

[b]Selenium effluent concentration based on pilot studies at DWR facility in Los Banos, California, and Fluid Systems in San Diego, California.

[c]Capital Investment does not include RO reject disposal.

[d]Costs shown in $/Kgal are in terms of feedwater to the plant. All capital costs are 2nd quarter 1985. Capital charge is based on annual interest rate of 6 percent, amortized over 20 years

[e]Operating costs are based on data given on Table IX-2. Power costs are based on 0.075 $/kWh.

[f]All costs shown are based on 87.5 percent recovery in the RO unit.

[g]Product water credit from resale is not included.

Source: CH2M Hill (1986).

$.0067/kWh (CVP) was significant, amounting to about $260/acre-foot (see figure I-12).

The commercial rate of $.075/kWh was used because the treatment facilities would not likely be CVP project facilities. If Congress should decree that treatment facilities operations are to be considered project operations and not customer operations, then the cost analysis would be based on project power rates. Presently, all CVP power is committed; what is not needed for CVP operation is committed by contract to Western Area Power Administration (WAPA) customers, so additional project energy needs would result in less energy available for existing customers, with the shortfalls being made up by purchasing more commercial energy at higher cost.

RO recovery rates (between 87.5 and 75 percent recovery) have little effect on the unit cost if Class II ponds are used (i.e., the 87.5 and 75 percent curves on figure I-12 nearly overlie each other). If Class I ponds are used for wastestream disposal, the unit costs are higher for 75 percent recovery than for 87.5 percent recovery.

Other RO studies and related cost estimates need to be discussed because of: (1) high costs reported in the CH2M Hill study, and (2) uncertainty that RO desalting of drainage water is indeed costly.

In reviewing the draft CH2M Hill report on RO, A. Ford (1986) urged consideration of operation at supersaturated calcium levels and a two-stage plant with a product recovery of 75 percent. Operation at supersaturated levels was not recommended by CH2M Hill because of a perceived high risk of

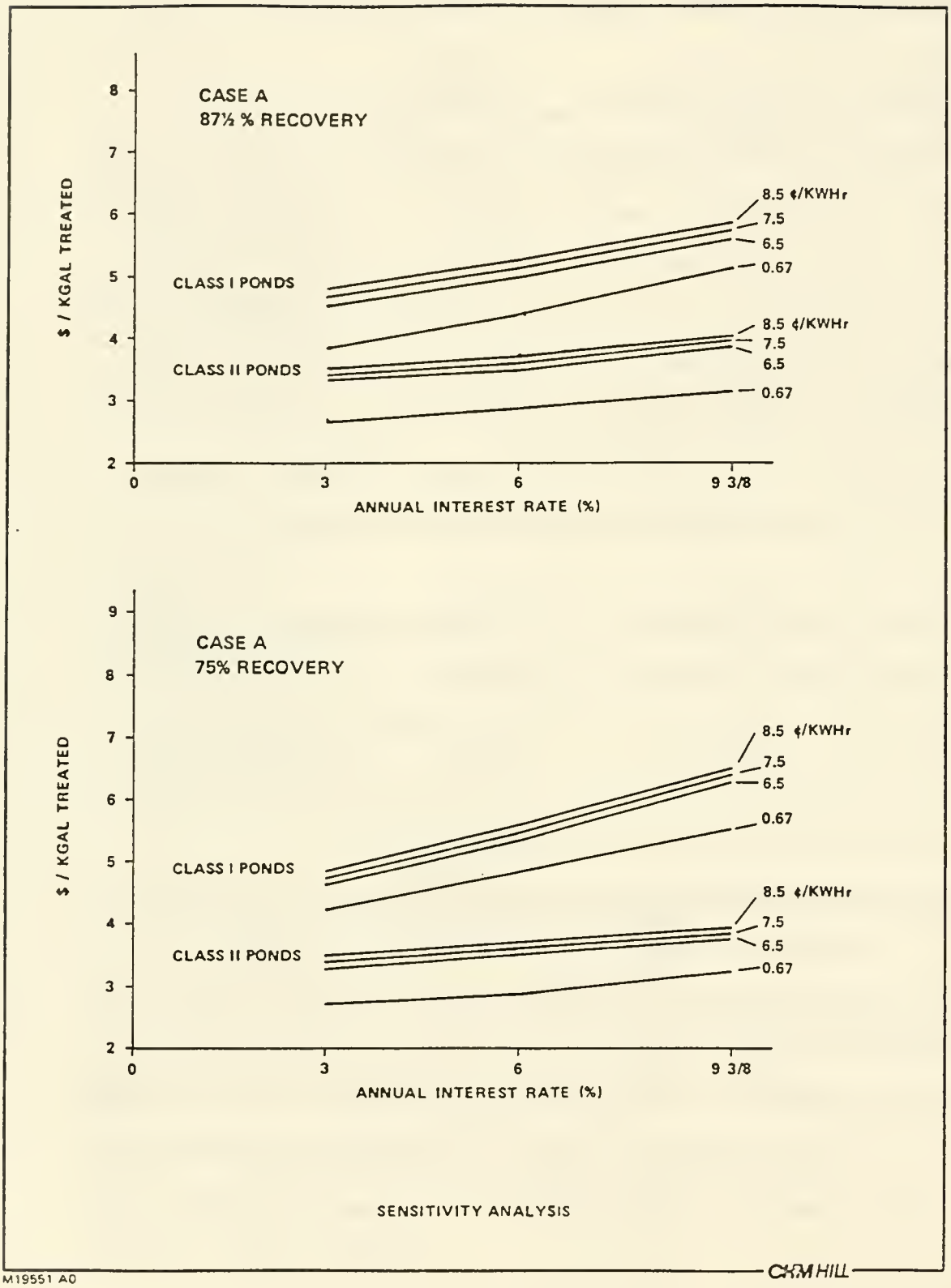


Figure I-12. Sensitivity analysis.
Source: CH2M Hill (1986).

scale formation from the high levels of calcium and sulfate. Nevertheless, adjustments to the CH2M Hill costs for supersaturated operation would result in a feedwater cost of about $800/acre-foot (not including disposal cost). Even this hypothetical revision for supersaturated operation did not substantially revise the RO costs and affordability by any major order of magnitude.

The USBR's Yuma Desalting Test Facility (YDTF) for desalting Wellton-Mohawk irrigation drainage water provides some insight on large-scale desalting costs. Construction is proceeding on an RO desalting plant originally sized at 96 Mgal/d, with an initial installed capacity of 72 Mgal/d (Trompeter, USBR, 1987). Initial average annual delivery of product water at 295 mg/L, TDS, is expected. This flow will be blended with raw drainage water to develop a total of 78,000 acre-foot/yr of blended water for delivery to the Colorado River.

Based on (1) the annualized cost of $326/acre-foot for the $210 million capital cost, and (2) operational cost projections of about $300/acre-foot based on the YDTF experience, the projected cost for the full-scale Yuma desalting facility would be about $626/acre-foot of feedwater. However, because the product water is 295 mg/L, TDS, allowance is made for blending raw water to allow a blended quality of 550-600 mg/L, TDS (i.e., comparable TDS quality of the product water in the CH2M Hill study). With this allowance, the unit cost for 550-600 mg/L water was estimated to be about $574/acre-foot, as compared to $626/acre-foot for 295 mg/L product water.

On the other hand, the chemical quality of San Luis Drain water is of significantly inferior quality compared to the Wellton-Mohawk Canal water. (See tables I-1 and I-5.) Note that the TDS and calcium levels in the Yuma feedwater are only about one-third of that in drainage water in the San Luis Drain. Consequently, on the basis of comparison of costs projected for the Yuma desalting plant, the desalting cost estimated by CH2M Hill ($1,090/acre-foot) appears to be within order of magnitude.

The California Department of Water Resources commenced start up of its Los Banos Demonstration Desalting Facility in October 1982. Its objective was to demonstrate various pretreatment processes (including RO brine regeneration described as Case C by CH2M Hill) for the desalting of drainage water in the San Luis Drain at a conceptual commercial size desalting plant. However, DWR's operating and capital cost data are not presently available. DWR states that a report on the Los Banos demonstration project will be produced soon.

The marketing of the product water is one of the principal advantages of desalting over other treatment processes, since it produces a product water acceptable for the widest range of reuse. Accordingly, it is appropriate to discuss the issues involved in the marketing of the product water because the sale of the water will directly reduce the overall desalting cost.

The quality of the product water for Case A, as projected by CH2M Hill, is of moderate and inferior quality, respectively, for domestic and

Table I-5. Wellton-Mohawk Canal Water and Pretreatment Composition at Yuma Desalting Test Facility

Parameter[a]	Concentration	
	Raw Canal Water	Pretreated Water
pH, units	8.00	9.74
TDS	3,332	3,235
Conductivity, umhos/cm	5,740	5,284
Silica	28.1	19.4
Calcium	228	118
Magnesium	90	71.6
Sodium	946	920
Potassium	8.5	8.1
Iron, total	0.35	ND[b]
Manganese, total	1.2	ND[b]
Strontium	3.4	1.99
Bicarbonate (as HCO_3)	433	14.2
Carbonate (as CO_3)	ND[b]	13.0
Sulfate	922	918
Chloride	1,195	1,170

[a]Expressed as mg/L unless otherwise noted
[b]ND = Not Detected

Source: [Trompeter, 1977]

agricultural uses, the main potential beneficial uses for the product water (see table I-6). The TDS level of 650 mg/L exceeds the USPHS secondary maximum contaminant level of 500 mg/L, TDS, for public water systems (U.S. Federal Register, 1979).

Agricultural use of the product water would be seriously hampered by the boron content. CH2M Hill's recommended Case A process lowers the boron level from about 15 mg/L to about 7-8 mg/L, but even at this lower range boron remains a threat to productive plant growth. CH2M Hill reported that boron removal with boron-specific ion exchange resin was considered to reduce boron to less than 0.5 mg/L. However, such treatment was dropped because the ". . . treatment plant capital and operating costs would be substantial." Instead, blending with low boron level freshwater was suggested as a viable method to reduce boron to acceptable levels.

Sale price of the product water is highly uncertain, especially in view of its quality. The marginal cost of water, or the cost to produce the next increment of water at the next stage of development, may be a reasonable basis to define the value of the product water. According to a DWR study investigating potential offstream storage of California State Water Project (SWP) water in Los Banos Grandes, the cost of water produced would range from under $100/acre-foot to over $225/acre-foot, depending on the method of reservoir operation (DWR, 1985). By contrast, the unit cost of water developed through the various alternatives for Delta water transfer ranged from about $40 to $70/acre-foot (DWR, 1983). DWR has reported that the financial equivalent unit cost of water, which relates

Table I- 6. Reverse Osmosis Stage Concentrations
Lime/Soda Softening (Case A)

Constituent	Units	Stage One Influent	Stage One Concentrate	Stage One Permeate	Stage Two Concentrate	Stage Two Permeate	Stage Three Concentrate	Stage Three Permeate	Overall Permeate
Na/K	p/m	2,919	5,721	117	11,156	286	22,107	669	176
Ca	p/m	30	60	0	119	1	230	2	2
Mg	p/m	243	484	2	960	7	1,857	19	12
Alk	p/m $CaCO_3$	10	17	4	26	9	33	18	7
SO_4	p/m	5,010	9,970	50	19,791	150	38,650	396	201
Cl/NO_3	p/m	1,550	3,038	62	5,924	152	15,987	355	155
SiO_2	p/m	14	27	1	49	.4	92	10	3
B[a]	p/m	14.5	23.4	5.4	38	8.8	62	14.3	7.6
Se	p/b	325	650	0	1,298	1	2,579	3	3
TDS	p/m	9,793	19,346	240	38,071	614	73,822	1,480	640
Pressure	lb/in^2g	450							
Flowrate	Mgal/day	9.93	4.96	4.96	2.48	2.48	1.24	1.24	8.68

[a]Boron concentrations are calculated from the following formulae:

$$\frac{Cp}{Cf} = \frac{1-(1-k)^{1-r}}{k} \qquad \frac{Cb}{Cf} = \frac{1}{(1-k)^{r}}$$

Where Cp, Cf, Cb = concentration in permeate, feed, and brine
k = Water recovery fraction (50 percent per stage)
r = Fraction rejected (.70 for TFC membranes)

Source: CH2M Hill (1986).

the yield of the project to all costs including financing charges, developed through water banking in the Kern River fan would be $70/acre-foot of firm yield (DWR, 1987).

Even allowing a liberal $250/acre-foot price tag for the product water despite its water quality deficiencies, the net unit costs for the product water under Case A amounts as follows:

Net cost for desalting = $840/acre-foot (i.e., $1,090 -250)

Net cost including
Class II waste ponds = $990/acre-foot (i.e., $1,140 -250)

Net cost including Class I
waste ponds= $1,400/acre-foot (i.e., $1,650 -250)

Transportation of the product water is also a potentially difficult problem. The most likely potential market for the product water is in southern California--San Diego, for example--where high municipal demand is reflected in a greater ability and willingness to pay for the water. (Incidentally, the TDS level in the drinking water supplies in San Diego County commonly exceeds 500 mg/L. Colorado River water, a large part of the water used in the county, has a TDS level of about 750 mg/L.)

However, it is doubtful that the product water could be transported to a southern California market in the California Aqueduct even if it had excess capacity. The State Water Project (SWP) has certain water quality objectives stated in its water supply contracts (table I-7) (DWR, 1965). The TDS (640 mg/L) and boron (7 mg/L) levels in the product water would substantially exceed the objective limits, especially for boron, and would

Table I-7. State Water Project Water Supply Contract Water Quality Objectives*

Constituents	Unit	Monthly Average	Average for any 10-Year Period	Maximum
Total Dissolved Solids (TDS)	ppm	440	220	--
Total Hardness (as $CaCO_3$)	ppm	180	110	--
Chlorides	ppm	110	55	--
Sulfates	ppm	110	20	--
Boron	ppm	0.6	--	--
Sodium Percentage	%	50	40	--
Fluoride	ppm	--	--	1.5
Lead	ppm	--	--	0.1
Selenium	ppm	--	--	0.05
Hexavalent Chromium	ppm	--	--	0.05
Arsenic	ppm	--	--	0.05
Iron and Manganese together	ppm	--	--	0.3
Magnesium	ppm	--	--	125
Copper	ppm	--	--	3.0
Zinc	ppm	--	--	15
Phenol	ppm	--	--	0.001

*Source: DWR Bulletin No. 141 (1965).

therefore probably be unacceptable for transport in the California Aqueduct. Of course, there may be other viable uses and markets.

Two basic findings emerged from the reverse osmosis study by CH2M Hill as follows:

o RO desalting of drainage water will be costly and will crucially rely on effective pretreatment. According to the CH2M Hill study conducted under contract for the SJVDP, the unit costs for the recommended off-the-shelf method to desalt drainage water in the San Luis Drain amounted to:

Unit cost for desalting = $1,090/acre-foot

Unit cost including Class II waste ponds = $1,140/acre-foot

Unit cost including Class I waste ponds = $1,650/acre-foot

o Marketing of the product water will help reduce the overall cost of desalting. However, the product water will be of moderate quality for domestic use and inferior quality for irrigation. There will probably be some problems in having it transported to southern California, the likeliest potential market for the water.

At the present the reports for the reverse osmosis studies by the California Department of Water Resources at Los Banos are still under preparation. When available, the operational features and cost for treatment will provide valuable information on the applicability of reverse osmosis as a treatment process for drainage waters.

Cogeneration Systems

A cogeneration/evaporator/crystallizer process that has innovative features for drainage management has been proposed by Coy (1987) of URS

Corporation, working with Resources Conservation Company. The main objective of this proposal is the disposal of salts from drainage water.

Drainage water would be desalted in evaporators to produce a relatively pure water and a salt blowdown. The blowdown would be fed to crystallizers and flash dryers to produce salt in solid form. Heat would be needed for the process, and a power plant using natural gas is proposed.

Preliminary studies indicated that sufficient revenue may be generated from the sale of surplus electrical power and salt to offset the capital and operating costs for the desalination plant. The proposal is at an early conceptual state, and further work has been recommended, including the integration of agroforestry systems for the production of biomass as a basic energy source. At this time, a study has been initiated by the Westlands Water District with Resources Management International for a review of the process to detect any major obstacles before initiating a detailed engineering evaluation of the concept.

ASSESSMENT OF TECHNOLOGY

The various treatment technologies under study for the management and control of drainage represent an advancement in the state of the art. A summary of the present status in the development of the most viable processes under study is shown in table I-8. It is noted that several of these processes are or will be considered for process patent applications. These include the anaerobic bacteria treatment (Binnie California Inc.), microalgal bacterial (Oswald), ferrous hydroxide (U.S. Bureau of Reclamation), selenium selective resins (Boyle), and selenium

Table I-8. Drainage Treatment Studies

Process	Level of Development	Findings
Anaerobic Bacterial (Binnie Calif.)	Experimental, pilot - continuous flow	Removal: Selenium up to 99% Heavy metals - substantial removal
Microalgal Bacterial (UC Berkeley)	Experimental, laboratory - batch; pilot - continuous flow	Selenium removal up to 95%, produces methane
Facultative Bacterial (US Bureau of Mines)	Experimental, laboratory - batch and continuous flow	Selenium removal up to 96%
In-Situ Immobilization (Lawrence Berkeley Lab)	Experimental, pilot - field	Selenium immobilization
In-Situ Volatilization (UC Riverside)	Experimental, laboratory; pilot - field plots	Selenium volatilization to atmosphere
In-Situ Attenuation (UC Riverside)	Experimental, laboratory - bench	Attenuation observed
Chemical (US Bureau of Reclamation)	Experimental, laboratory - batch; pilot - batch	Selenium removal up to 99+% - other heavy metals removed
Iron Filings Adsorption (Harza Engineering)	Experimental, pilot - continuous flow	Selenium removal varies
Ion Exchange Resin (Boyle Engineering)	Experimental, laboratory - batch	Selective selenium removal potential observed
Reverse Osmosis Desalting (CH2M Hill)	Proven technology, conceptual level study	Removal: TDS - 94% Selenium - 99+% Boron - 48%

volatilization (Frankenberger). Others may be added to this list as their development progresses. This listing is an indication of the intensive and innovative approach required to solve the drainage problems in the San Joaquin Valley.

In the SJVDP, the assessment of treatment technology faces certain limitations in implementation of the study program. This is an administrative issue related to the level of funds available for treatment studies and the time to complete these studies within the timeframe of the SJVDP.

As the several treatment processes are advanced and the more promising ones are taken to the field for testing, there will be need to consider pilot prototype plants. The costs to conduct typical pilot plant studies are much greater than laboratory bench scale or miniscale plant studies. The experiences of the Binnie anaerobic bacterial process can attest to this problem, since they are presently deciding whether or not to proceed with a larger pilot prototype plant, estimated to cost several million dollars. The alternative would be to use miniscale plants under field conditions to gain basic performance data and information on selected processes. However, there is some risk, particularly in biological systems, in deriving technical data and information from miniscale plants.

Closely related to the selection of pilot plant size is the time limitation of the SJVDP, which is scheduled to be completed in Fiscal Year 1990. The design, construction, and operation of a typical prototype plant will take 24 to 30 months. With provisions for analysis and report

preparation, the schedule for any study starting in Fiscal Year 1989 (Oct. 1989), the earliest time when new funds would be available, will seriously constrain timely completion of test programs. Therefore, any plan for pilot plant studies must consider first these constraints before initiating investigations.

The various treatment processes under investigation must be assessed in relation to potential field application, in which location is an important factor. Each technical system has characteristics which may guide its application. For example, in-situ processes are for application at selected sites, where control is needed. The iron filings and ion exchange processes may have their best potentials applied at locations where high levels of contaminants are found in the local drainage system. These could be medium sized systems which are more amenable to farm or district level application, where operational requirements can be minimized. For biological processes, large centralized plants are envisaged, since the operational and maintenance requirements are more complex. Thus, in the assessment of any treatment technology, the locational aspects must be melded with the specific characteristics of the processes itself. To provide a broad range of utility, the technology must be developed to integrate the needs at different locations. For this reason, several processes or combination of processes must be developed and reliance should not be placed on any single process, particularly at this stage of the program.

Closely related to the development of treatment processes is the need to evaluate any potentially adverse impacts from waste byproducts. These can include gases, concentrated liquids, and solid forms. As each potentially viable treatment process is developed, the byproducts and potential impacts can be identified and any related problems can be addressed, as part of the overall development process. This becomes an important assessment of the environmental impact of the specific technology that must be evaluated before it becomes fully acceptable for field application.

There remains needed efforts to develop criteria for comparing the various treatment processes in terms of effectiveness, reliability, costs, and utility, in addition to environmental consequences. Until each technology is developed to a stage wherein effectiveness and affordable cost are clearly defined, the development of comparative criteria can not proceed with reliability. It is not believed that the several promising processes identified to date have attained this level of development and therefore comparison of methods must be a future effort by the SJVDP.

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APPENDIX A

ASSESSMENT OF TREATMENT TECHNOLOGIES

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APPENDIX A
ASSESSMENT OF TREATMENT TECHNOLOGIES[1]

INTRODUCTION

The following assessment of treatment technologies is based on and largely abstracted or taken verbatim from a report for the State Water Resources Control Board (SWRCB, 1987) prepared by Professor David Jenkins of the University of California, Berkeley. Appreciation is expressed for his contributions to this Appendix and to the SWRCB for the funding of his study.

The ability of a waste treatment process to remove pollutants depends largely on the waste composition. Accordingly, Professor Jenkins, in his review of treatment technology, based his assessment on the drainage wastewater of the typical compositions shown in tables A-1 and A-2. He focussed his review on the four constituents selected by the State Water Resources Control Board (SWRCB, 1987) in its recommendation for setting water quality objectives in the San Joaquin River Basin for the regulation of drainage. These are salinity (TDS), selenium, boron, and molybdenum but Appendix A covers only the trace elements. Desalination (TDS reduction) is covered in Appendix B.

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1. Source: "Assessment of Treatment Technologies, Appendix H," State Water Resources Control Board Technical Committee Report, Regulation of Agricultural Drainage to the San Joaquin River (May 1987). Professor David Jenkins, University of California, Berkeley, and Western Consortium for Health Professionals.

SELENIUM REMOVAL

The chemical speciation of selenium and the chemical matrix of the wastewater are very important in selenium removal. In the waste streams of interest, selenium largely occurs as the selenate anion (SeO_4^{2-}). Minor amounts are also present as selenite (SeO_3^{2-}). These selenium forms are usually in combination with Ca, Mg, or other ions. Significant amounts of sulfate, which is chemically similar to selenate, are also present. The presence of nitrate is significant when the removal of selenate involves microbial reduction methods since nitrate must be reduced before selenate is reduced.

Table A-1. Typical composition of agricultural surface and tile drainage

Constituent	Units	Average	Maximum	Minimum
Sodium	mg/L	513	718	321
Potassium	mg/L	5.3	9.0	4.0
Calcium	mg/L	226	330	142
Magnesium	mg/L	67	119	42
Alkalinity ($CaCO_3$)	mg/L	164	285	74
Sulfate	mg/L	992	1470	598
Chloride	mg/L	508	728	308
Nitrate	mg/L	84	118	58
Boron	mg/L	6.8	10	4.7
EC	umho/cm	2770	3800	1700
pH (field)		7.8	8.2	7.5
TDS	mg/L	2625	3850	1620
Suspended solids	mg/L	286	1190	17
Total organic carbon	mg/L	26	40	13
COD	mg/L	8	14	6
BOD	mg/L	3	8.8	1.4

Source: "San Joaquin Valley Drainage Monitoring Project," California Department of Water Resources, Fresno District, 1976-1983. For surface drain DPS-3235, location 125/12E-05D. Nr. Dos Palos. Samples are grab samples.

Table A-2. Typical agricultural tile drainage composition (San Luis Drain at Mendota, SLDC41)

Constituent	Units	Average	Maximum	Standard deviation
Sodium	mg/L	2230	2820	200
Potassium	mg/L	6	12	1
Calcium	mg/L	554	714	25
Magnesium	mg/L	270	326	20
Alkalinity (as $CaCO_3$)	mg/L	196	213	10
Sulfate	mg/L	4730	6500	400
Chloride	mg/L	1480	2000	100
Nitrate/Nitrite (as N)	mg/L	48	60	5
Silica	mg/L	37	48	4
TDS	mg/L	9820	11600	500
Suspended solids	mg/L	11	20	3
Total organic carbon	mg/L	10.2	16	3
COD	mg/L	32	80	8
BOD	mg/L	3.2	5.8	1.0
Temperature[a]	deg C	19	29	--
pH	--	8.2	8.7	0.2
Boron	ug/L	14400	18000	2000
Selenium	ug/L	325	420	90
Strontium	ug/L	6400	7200	500
Iron	ug/L	110	210	50
Aluminum	ug/L	<1	<1	--
Arsenic	ug/L	1	1	--
Cadmium	ug/L	<1	20	--
Chromium (total)	ug/L	19	30	--
Copper	ug/L	4	5	--
Lead	ug/L	3	6	--
Manganese	ug/L	25	50	--
Mercury	ug/L	<0.1	<0.2	--
Nickel	ug/L	14	26	--
Silver	ug/L	1	<1	--
Zinc	ug/L	33	240	--

Source: USBR "San Luis Drain, Inflow and Water Quality Data," June 1985.

In waters such as those encountered in drainage flows to the San Joaquin River, selenate is, in general, more difficult to remove than selenite because of the greater solubility of metal salts as selenates and because of its chemical similarity to sulfate. Chemical, physical, and microbiological methods of selenium removal have been proposed.

Chemical Precipitation Methods

Sorg and Logsdon (1978) examined the effectiveness for selenium removal of several of the chemical precipitation methods used in municipal water treatment. Coagulation with ferric sulfate (20-30 mg/L at pH $\leq$7), in jar tests and in a pilot plant, reduced selenite levels from 30 ug/L to 10 ug/L. At the same levels of selenate, only 10 percent removal was obtained using either ferric sulfate or alum. Lime-soda softening at optimum pH removed 35-45 percent of these levels of selenite, but less than 10 percent of selenate.

Merrill et al. (1986) reported on pilot plant studies of ferric chloride addition to coal-fired electric powerplant ash pond effluent for selenium removal. Coprecipitation or adsorption onto the ferric oxyhydroxide was the proposed removal mechanism. Earlier work by the Electric Power Research Institute (EPRI) (unpublished and 1985) showed >80 percent removal of selenite (initial concentration 120 ug Se/L) at iron doses in the range 14-56 mg Fe/L at pH values between 6 and 7. Under the same conditions, selenate removal was less than 10 percent. In pilot plant studies selenite removals were found to be of the same order and were optimum below pH 6.2. Selenite adsorption was complete in a 2-minute

detention time rapid mix unit. Some conversion of selenite to selenate (approximately 5 ug Se/L) was detected; the authors suggest this may have been due to oxidation by ferric ion.

On the basis of these results and because the majority of the selenium in agricultural drainage water is present as selenate, it can be concluded that precipitation methods without prior conversion of selenate to selenite would be ineffective techniques.

Adsorption (Physical)

Sorg and Logsdon (1978) demonstrated in four tests that up to 100 mg/L of powdered activated carbon removed less than 4 percent of 30 ug/L and 100 ug/L selenite and selenate. Theim and O'Connor (1977) had previously reported similar results. Sorg and Logsdon (1978) showed that treatment with activated alumina resulted in 95 percent removal of 300 ug/L of both selenite and selenate from "spiked" distilled water; when a hard ground water was used, the selenite removals fell to between 62-68 percent and there was no selenate removal. The reduction in selenium removal efficiency was thought to be due to sulfate competition for adsorption sites on the activated alumina. This supposition was confirmed by Trussel et al. (1980), who showed that both the adsorption capacity and the kinetics of adsorption for selenite were much more favorable than for selenate. Because of the sulfate competition, sulfuric acid is not suitable for activated alumina regeneration when selenate removal is desired.

An adsorption process (the Harza process) recently patented by Mayenkar (1986) uses beds of iron filings to remove selenium from agricultural drainage water. The patent itself does not address the removal of selenium (rather, the removal of metals such as iron, nickel, zinc, copper, lead, chromium, mercury, and arsenic is discussed). Treatment units employing this process have been installed in 1985 on agricultural tile drain sumps in the Panoche Drainage District, California.

Falaschi (1986) of the Panoche Drainage District supplied raw data and information from these studies, which were assessed. Based on the Phase I study, the following conclusions were drawn:

a. Iron filing bed performance appears to be related to overflow rate, (i.e., the velocity of wastewater flow through the bed). This indicates that "kinetic or diffusion" control of the selenium removal process exists.

b. An overflow rate of 0.054 gal/min/ft^2 seems to lead to rapid breakthrough of selenium into the column effluent.

c. At an overflow rate of 0.013 gal/min/ft^2 selenium breakthrough was not obtained during the experiments (i.e., after a period of approximately 3 months).

d. Selenium breakthrough seemed to be occurring at an overflow rate of 0.02 gal/min/ft^2 by the end of Phase I.

e. For the conditions of Phase I, it appears that waste flow velocities of less than 0.02 gal/min/ft^2 are required for an

extended column life. Based on these data no prediction of an ultimate life prior to exhaustion can be made at this overflow rate.

f. Within the range tested, column depth did not seem to have an important effect on selenium removal performance.

g. Because data on: (1) Selenium speciation and distribution in the columns, and (2) mass balances of selenium were not available, the removal mechanism for selenium could not be determined.

In the Phase I study, problems were encountered in column operation as the iron filings became "cemented" together at the point of first contact between the wastewater and the iron filings. This led to plugging of the columns, and because it occurred at the bottom of the bed of iron filings, it was difficult to disrupt.

Phase II experiments employed downflow columns so that the cemented region would be at the more readily accessible surface of the columns. Furthermore, the location of the columns was changed so that a drainage wastewater containing higher selenium levels could be studied. From the Phase II operations thus far, it can be concluded that selenium removals again seem to be a reflection of overflow rate (waste application rate) and are generally consistent with the data produced in Phase I.

Cementation and the attendant column plugging have again occurred and have required harsh measures (such as breaking with an iron bar or hitting with a sledge hammer) to alleviate them.

Another observation made during a visit by Professor Jenkins to the Phase II operating site was the yellow-orange tint of the column effluents. This suggested the presence of ferric iron and was supported by some data from Phase I where effluent Fe concentrations in the range 11-59 mg/L were measured. Suspended solids levels in Phase I column effluents were measured in the range <1-104 mg/L.

The mechanism by which this process removes selenate is not clear. Tyndall (1986) claims that contact of the iron filings with oxygenated wastewater or other aqueous media (such as makeup water) produces an "activated" surface. This "activated" surface combines with (adsorbs) and immobilizes selenium to an extent that, it is claimed, will not allow leaching during extraction tests.

An earlier patent (Baldwin et al., 1983) describes a process (the Kerr-McGee process) by which selenate can be reduced (to possibly selenite and selenium metal) by contact with iron filings in a solution with a pH of less than 6 and preferably in the range 3.0-5.5. The reduced selenium forms are hypothesized either to form a precipitate with the ferrous hydroxide formed during selenate reduction and reaction with water, or to combine to the iron metal/metal oxide surface itself. This process was developed to remove selenate from uranium mining waste. It bears many similarities to the Harza process; in fact, the only obvious difference would seem to be the pH at which the contact between the iron filings and the wastewater is made.

Using the oxidation reduction potentials (Latimer, 1952), it is possible to write a series of hypothetical oxidation reduction reactions that could account for the observed removal of selenate and production of ferric iron in the Harza process effluent. Furthermore, the cementation of the iron filings observed in the experiments may be explained by the formation of precipitates of ferric hydroxide and, to a lesser extent, ferric selenite. Taken together, such a mechanism could be construed to mean from: (1) The observation of cementation at the point of initial contact of waste in the column, and (2) the relationship of selenium to the surface application rate of the waste, that selenium removal is taking place just at the surface of the columns only.

Brown (1986) collected influent and effluent grab samples from Train III of the Phase I tests of the Harza process at the Panoche Drainage District. He concluded that reduction of nitrate to nitrite was occurring in the column (decrease from 38.2 ug/L to 10 ug/L through the process). It is possible that the iron filings provide a media for biological growth and that oxidized nitrogen removal may be occurring through denitrification and/or microbial growth.

Chemical Reduction of Selenate

The chemical reduction of selenate and selenite by sulfur, sulfide, and sulfur dioxide (sulfite) has been demonstrated for concentrated solutions and/or high temperatures (Feigl and West, 1947). Selenate reduction appears to be interfered with by sulfate. Batchelor (1986) is now determining whether acceptable selenate reduction rates using sulfide

can be achieved for application to low selenium levels such as those found in agricultural drainage waters. One of the areas that this research will follow is to seek an effective and environmentally acceptable catalyst for these reactions.

Ion Exchange

As with adsorption on activated alumina, the selective removal of the selenate from agricultural drainage wastewater by ion exchange is severely impacted by the presence of large amounts of chemically similar sulfate. Indeed, Maneval et al. (1984) concluded that the ion exchange behavior of sulfate and selenate on the strong base resins Dowex 1X8 and 2X8 at representative drinking water concentrations are identical. Thus, selenate removal can be achieved by a strong base ion exchange if the sulfate is also removed (Hermann, 1985). Various ion exchange techniques have been suggested for selective selenate removal; however, none has been used successfully in the presence of large amounts of sulfate. Included among these techniques are the use of:

Electron exchange resins. Resins that act as catalysts for the reduction of selenate or selenite to elemental selenium. Functional groups could be hydrazine, 8-hydroxyquinoline, hydroquinone, hydroxyoxime, etc. These resins initially showed promise (Murphy, 1985) when older batches were used but did not perform well with fresh batches of resin (Altringer, 1986).

Natural zeolites. These materials have been examined by the U.S. Bureau of Mines, thus far with disappointing results (Altringer, 1986).

Glass media ion exchange resins. Investigations are being conducted at the Catholic University of America in Washington, DC. These resins (Durasil resins) are based on a porous vitreous silica medium and are being developed for use in decontaminating radioactive wastes (Barkatt, et al., 1985). There is a possibility that resins of this family can be developed to have some selectivity for selenate over sulfate (Litowitz, 1986).

Boron exchange resin. From the Murrieta Farms pilot plant experiments (Squires, 1986) at Mendota, California, a glycol-based resin used for borate removal, appears to have some capacity for removing selenium (form unknown) from the effluent from the anaerobic reactor-cross flow filter system.

Weak-acid cation exchange resin. A weak-acid cation exchange resin in the ferric form was found by Maneval et al. (1984) to selectively remove selenite (1.0 mg/L) in the presence of 260 mg sulfate/L in laboratory experiments. The ferric ion releases gradually from the ion exchange column and precipitates selenite.

Reverse Osmosis

Reverse osmosis (RO) is a membrane process in which solutes can be separated from water by applying pressure to a solution so that the water is forced through the membrane (against the osmotic pressure) and the solutes are retained. The process produces a desalted water (product water) and a salty solution (reject brine). Many factors influence the rejection of solutes by RO membranes. These include product water

recovery, nature of the solute, nature of RO membrane, pH, presence of other electrolytes, etc.

Marinas and Selleck (1985) reviewed the literature on selenium removal by RO (Sorg and Logsdon, 1978; Fox, date unknown; Wilmoth et al., 1979; Huxstep 1982; Sorg and Love, 1984) and concluded that the reported work indicated that selenite removal was less than selenate removal at low pH, but that an exact prediction of selenate rejection was currently not possible. The behavior of organic selenium compounds in RO is unknown. Notwithstanding these unknowns, Marinas and Selleck (1985) crudely estimated roughly that the RO section of the Los Banos Desalting Facility (California Department of Water Resources, 1983) would reject selenium (selenate) to the extent of 94 percent. This would produce a product water with a selenium level of 18 ug Se/L from a feed water selenium concentration of 300 ug Se/L.

Marinas and Selleck (1986) assessed the performance of the Los Banos Desalting Facility RO units over an approximate 1,500-hour period of operation in the summer of 1985. The system produced a product water selenium level of 1.2 ug Se/L from an influent level of 266 ug Se/L representing a 99.55 percent rejection rate (table A-3). In its conceptual design of an RO desalting plant for the San Luis Drain water, CH2M Hill, Inc. (1986) indicate that for product water TDS levels of 550-650 mg/L, selenium levels will be below 10-20 ug/L.

Table A-3. Water analysis and solute passage after approximately 1,500 hours of operation of the 13,000 gal/d RO unit operated at Los Banos Desalting Demonstration Facility, Los Banos, California
(water temperature = 24-25 °C; pH = 4.7-5.8; and product recovery = 43-44%

Constituent	Feed water	Brine water	Product water	Percent solute passage
SO_4^{2-} (mg/L)	4,410	7,820	11	0.25
Cl^- (mg/L)	1,430	2,480	37	2.59
NO_3^- (mg/L)	206	336	34	16.5
Ca^{2+} (mg/L)	3	4	0	--
Mg^{2+} (mg/L)	22	32	0	--
Na^+ (mg/L)	3,100	5,480	42	1.35
K^+(mg/L)	15	26	0.2	1.33
Alk. (mg/L as $CaCO_3$)	55	91	4	7.3
H_3BO_3 (mg/L as B)	14	18	10	71
SiO_2 (mg/L)	8.0	14	0.0	--
Se (mg/L as Se)	0.266	0.520	0.0012	0.45
TDS (mg/L)	9,320	16,400	145	1.56
Conduct at 25 °C (mhos/cm)	12,400	20,300	228	1.84

After Marinas and Selleck (1986)

Microbiological Methods

Microorganisms common in the soil and in natural waters can take up selenium compounds and can mediate oxidation-reduction reactions involving selenium species. Of particular interest to the removal of selenium from agricultural drainage wastewater are those reactions in which selenate is reduced usually either to selenide or to selenium metal, or those which allow for the incorporation of selenium into organo-selenium compounds. Several candidate processes incorporating the microbial reduction of selenium are in various stages of investigation.

Microbial process for removal of selenate. Kauffman, et al. (1984), proposed a microbial treatment process for selenate removal from uranium mine waters in which organisms growing in soil columns (Chlostridium spp) reduced selenate to selenium metal, which was deposited inside the microbial cells (red deposits). The use of either 15-cm-deep soil columns or 30-cm-deep columns containing a 1:1 mixture of soil and sand, and a waste application rate of 90 L/m^2-day of a waste containing 1,300 ug/L selenate, reduced selenate to 12 ug/L. Increasing the waste application rate progressively to 540 L/m^2-day increased effluent selenate levels to 420 ug/Se/L. However, feeding 360 mg/L glucose to the soil columns, together with the wastewater, produced effluent selenate concentrations of 50 ug/L.

Field tests were conducted in 3.65 m-deep x 0.91 m-diameter soil columns. Depending on the soil used (either from below an algae pond already treating mine waste or from an alluvial source), the columns

reduced selenium levels to <50 ug/L at waste application rates of 80-160 L/m^2-day and added sucrose levels of 700 mg/L. It appeared that the conditions in these experiments were anoxic (if not anaerobic) because of the amount of degradable carbon source added and because the anaerobic organisms were identified as being active in selenium metal deposition (Chlostridium spp). Furthermore, the investigators reported the presence of sulfide in some of their columns.

The field scale results suggest that this process may be impractical for treating the San Joaquin Valley agricultural drainage water. Besides requiring high doses of organic carbon, the highest field-scale application rate of 160 L/m^2-day translates to 0.53 acre-ft/acre/day.

Aerobic conversion of selenate. Gersberg, et al., (1985) and Gersberg, (1986) with the San Diego Region Water Reclamation Agency has conducted laboratory-scale studies on the aerobic conversion of selenate to selenium metal. Gersberg indicated that some organisms possess a mechanism for detoxifying selenate by reducing it to selenium metal, which is deposited intracellularly; this reaction has been shown to be mediated for gram-per-liter levels of selenate by organisms of the genera Desulfovibrio, Chlostridium, and Pseudomonas in the presence of nitrate and in shake cultures open to the air. A carbon source such as glucose, acetate, or methanol was added to support microbial growth.

Recent work has been conducted on organisms immobilized on calcium alginate gel beads. At gram per liter levels of selenate, deposits of the red selenium metal have been observed in the microbial cells. Studies

utilizing selenate levels of 350-400 ug Se/L in agricultural drainage water have shown that detention times of 12-24 hours are required to produce selenate residuals of approximately 150 ug/L. Investigations with radioactive labeled selenate have shown that differences exist between microbial SeO_4^{2-} and SO_4^{2-} reduction pathways, whereas uptake rates and mechanisms are similar. Future plans are to scale up the immobilized organisms to a field scale reactor and to develop genetically altered organisms capable of high selenate reduction rates for addition to a field scale reactor. Applications seen for this method are the use of immobilized organisms in flow-through reactors for treatment of agricultural drainage wastewater or the addition of these organisms to evaporation ponds.

Anoxic reduction of selenate. EPOC Agricultural Corporation is using anoxic conditions to effect the microbial reduction and insolubilization of selenate from agricultural tile drainage water in a 5-10 gal/min pilot-scale plant at Murrieta Farms, California (Squires, 1986). This pilot plant consists of three reactors in series, the first two containing 1.5-inch rock media and the last an iron wool medium. A degradable carbon source is added to the agricultural drainage waste prior to entering the first reactor. Carbon sources used thus far have been methanol and a sugar beet manufacturing waste known as Steffan's solution. The first two reactors are upflow and the final reactor is downflow. Typical average hydraulic detention times in the reactors are 1.5-2.5 hours each.

Four fluidized sand bed reactors have also been used in series, each with a hydraulic residence time of 10-11 minutes. The carbon source is dosed to remove nitrate by denitrification. The nitrate levels are extremely high in the wastewater being treated at Murrieta Farms (values in the range of 130-160 mg NO_3-N/L have been reported), whereas the typical agricultural tile drain wastewater has NO_3-N concentrations of 40-60 mg N/L. With these high levels of nitrate, first-stage reactor effluent has varied from 1-60 mg NO_3-N/L, and second-stage effluent values have been in the range <1-2mg NO_3-N/L. The reduction of selenate to a variety of products, including selenium metal, dimethyl selenide, and an "insoluble organic selenium compound" apparently requires that nitrate be reduced previously. The influent selenate concentration has ranged from 350-500 ug/L; first-stage total selenium values are approximately 250 ug/L; the second-stage total selenium levels are ranged from 150-200 ug/L.

A significant reduction in selenium takes place in the third-stage reactor, with effluent total selenium concentrations reaching about 40-50 ug/L. The effluent from this reactor passes to a filtration step--in this case, a cross-flow microfilter. This filter is a pressure filter consisting of a tube of fabric internally precoated with a metal hydroxide. The filters are claimed to be capable of removing particles down to dimensions of 0.1 micron (EPOC Agricultural Corporation, 1985). Waste flows down the inside of the tube and is treated by passing through the precoat layer and the fabric tube. The retained solids are removed down and then out of the end of the tube and the filtering surface is thereby

continuously renewed. Following the filtration step, selenium concentrations have varied from <10-20 ug/L. The next step in the treatment train is an ion exchange step for boron removal using Amberlite IRA-743 resin (Rohm and Haas). It is claimed that this resin effects an additional "polishing" removal of selenium.

The microbial phases of this process train bear many similarities to the processes used at Firebaugh, California (Environmental Protection Agency, May 1971 and July 1971) for the denitrification of agricultural tile drainage wastewater during the late 1960's and early 1970's. Both processes used rock-filled upflow reactors dosed with methanol. One might conclude that the Firebaugh denitrification systems would also have been found to effect some degree of selenium removal had these measurements been made.

Both the Murrieta Farms and the Firebaugh denitrification units required removal of sludge made up of the biomass accumulated in the reactors from growth associated with the denitrification reaction to maintain their effectiveness. The recommended procedure for this solids removal at Firebaugh was periodic air injection either with, or followed by, flushing with water at rates higher than the typical operating rate. Note that if this were performed for the selenium removal version of this treatment process, sludge separation, handling, and processing units would be required.

As with the current selenium removal process, the Firebaugh study recommendations included the construction of a scaled-up plant to better

determine long-term operating characteristics and to enable designing the waste distribution system to overcome the hydraulic distribution problems encountered in the smaller pilot plant units. The possibility of investigating biomass support media other than rock was also mentioned. In the Firebaugh study recommendations, the use of synthetic plastic media was mentioned. Such media have been suggested for study at Murrieta Farms, as well as the possibility of using an expanded fluidized bed type of reactor system or of using suspended growth (i.e., anoxic activated sludge) systems.

In the Murrieta Farms operation it is recognized that agricultural drainwater is low in phosphate. For biological denitrification, especially of the very high nitrate values encountered there, phosphate is supplemented. In the Firebaugh studies the agricultural drainage waste was not supplemented with phosphate; effluent phosphorus levels of 0-0.5 mg/L were reported, suggesting that at times these units may have been phosphorus limited.

Current activities at the Murrieta Farms pilot plant include an investigation into the ability of the process to remove selenium at the high salt concentrations typical of evaporation ponds. These studies are being conducted in anticipation of applying the process on a side-stream loop from an evaporation pond to keep pond selenium levels below the currently regulated value of 1 mg/L as evaporation proceeds.

Ponding methods. Deep anaerobic ponds (14 feet) were investigated on a large-scale pilot plant in the Firebaugh study (Environmental Protection

Agency, 1971). Methanol was added to the influent wastewater to provide the necessary reductant. It was necessary to cover the ponds to maintain satisfactory anaerobic conditions. The pond performance was influenced significantly by temperatures between 12-16 °C. Nitrate reduction from 30 mg N/L to 2 mg N/L required a 60-day average hydraulic residence time and recirculation of some 25 percent of the effluent. Above 20 °C effluent recirculation was not needed, and for a reduction of NO_3-N levels from 15 mg/L to 2 mg/L, a 10-day hydraulic residence time was sufficient. While selenium measurements were not made in these studies, it is possible that some selenium insolubilization could have occurred, since NO_3-N levels similar to those experienced in the Murrieta Farms plant were achieved.

A so-called "integrated pond system" for removing trace elements, such as selenium, from agricultural drainage wastewater has been proposed (Oswald, 1985). The proposed process train consists of:

a. A facultative high rate pond.

b. An aerobic high rate pond.

c. Algae separation by coagulation with, for example, ferric chloride and dissolved air flotation.

d. Fermentation of the separated algae in an aerobic digester.

e. Recycle of CO_2 (and CH_4 combusted to CO_2) from digester gas to the influent to the pond system.

f. Mixing of algae digester effluent containing "reducing agents" (Oswald, 1986) to reduce selenate.

The integrated pond system is designed around growing 300 mg/L of algae (dry weight) on the agricultural drainage wastewater. To achieve this, additions of carbon (~77 mg/L), nitrogen (~3 mg/L) and phosphorus (2.6 mg/L) will be necessary. While the ability of the microalgae that grow in such a ponding system to take up selenium is not known, one can use data presented by Oswald (1985) to estimate this ability. From table III of Oswald's report, data are given (Saiki, 1984; Beck, 1985) for the filamentous algae and plankton growing in Kesterson Reservoir and for marsh pond algae at Los Banos (both growing on San Luis Drain water). Averaging the range of algae selenium contents from all these sources yields a value of 86 mg Se/kg dry algae. At a growth of 300 mg/L of algae, this selenium content would result in a maximum selenium removal of 26 ug/L. To provide the necessary removal of selenium, much higher selenium accumulation rates and/or algae production rates would be required. Thus, the "reducing agents" (Oswald, 1986) in the digested algae must be able to reduce the majority of the selenate to a more readily removable form.

Weres et al. (1985), propose the use of clay-lined (either natural or in place) engineered eutrophic ponds for selenium removal from agricultural drainage water. This proposal is made on the basis that such a pond would accumulate a layer of decaying organic matter at its bottom, which would provide a reducing environment capable of converting selenate to less soluble (and less mobile forms) such as selenite, selenium metal, organic selenium forms, and selenides. The proposal cites the experiences at Kesterson Reservoir, where selenate immobilization in organic sediments is

claimed to prevent its wholesale movement into the underlying ground water. Weres and coworkers suggest that enough phosphate would need to be added to maintain the pond in a "eutrophic state," and that iron salt addition may be required to form pyrite, with which selenides may coprecipitate. The ponds would be underdrained to collect "deselenified" water for further transport and disposal.

BORON REMOVAL

Since the equilibrium constant ($pK_{a,1}$) of boric acid is 9.3 at 25 °C, boron exists in agricultural drainage water as boric acid, H_3BO_3. Salts of boric acid are extremely water soluble. Because of these characteristics, boron is very difficult to remove from water by precipitation reactions and processes that rely on the presence of a charged species. Reverse osmosis removals of boron from agricultural drainage waters at the Los Banos RO desalting plant have been from influent concentrations in the range of 10-14 mg/L to effluent (product water) concentrations of 5-9 mg B/L. CH2M Hill (1986) suggests in its conceptual design of an RO desalting plant for the San Luis Drain water that product water will contain 7-8 mg B/L.

Conventional Processes

Conventional biological waste treatment processes and chemical coagulation with lime, ferrous, and aluminum salts are ineffective in removing boron (Waggott, 1969). The adsorption of borate on solids such as clays and soil minerals has been studied extensively (Metwally et al., 1974; Choi and Chen, 1979; Keren et al., 1981; Keren and Mezuman, 1981; Keren and O'Conner, 1982). However, such methods for boron removal from

agricultural drainwater could hardly be appropriate because this water has already passed through several feet of soil.

Kane and Anstadt (1971) reported that polysaccharides, such as starch and cellulose, form complexes with borate and could be used as the basis for an exchange resin. However, Okay et al. (1985), found such exchangers to be inefficient with capacities of only 0.3-0.54 mg B/g cellulose. Magnesium oxide (regenerated by heating) has been used as an adsorbent for borate (Krejcirik, 1968), but Okay et al. (1985) found this technique useful only for high concentrations of borate (>100 mg B/L), from which 70 percent removal was achieved. Other methods of boron removal (e.g., evaporation-crystallization, solvent extraction) are more applicable for the production of boric acid (Garbato, 1961; Garrett et al., 1963; Basol and Eren, 1975; Grinstead, 1972).

Ion Exchange

The only existing process that holds promise for high boron removal efficiencies is a specific ion exchange resin with a sorbityl functionality (Kunin, 1971). This resin, Amberlite IRA-743, manufactured by Rohm and Haas, has been in use for many years on an industrial scale in two plants for the removal of borate from magnesium chloride brines. These plants are located at the Dead Sea, Israel, and at Freeport, Texas (Dow Chemical Co.). The resin was also studied by Okay et al. (1985) for the removal of boron from boron mine drainage waters.

Rohm and Haas (1980) claim that for simulated agricultural drainage water (500 mg NaCl/L, 10 mg B/L) the capacity of the resin is

0.125 lb B/ft^3 resin, and an effluent of <1 mg B/L can be produced. For this performance, two-stage regeneration using 10 percent H_2SO_4 at 3 lb/ft^3 and 4 percent NaOH at 4 lb/ft^3 are employed. Similar data were obtained by Aerojet General (1970). With the same two-stage regeneration rates, resin capacity was 0.19-0.25 lb B/ft^3 at 1 gal/min/ft^3, 0.125-0.16 lb B/ft^3 at 2 gal/min/ft^3, and 0.031-0.063 lb B/ft^3 at 4 gal/min/ft^3.

The Murrieta Farms pilot plant for treatment of agricultural drainage wastewater incorporates an Amberlite IRA-743 ion exchange column for boron (and selenium) removal following the anaerobic reactors and the cross flow microfilter. Squires (1986) has reported that at flow rates of 0.6-0.8 gal/min/ft^3, effluent boron levels of <1 mg/L can be achieved with a resin capacity of 0.16 lb B/ft^3 using single-stage regeneration with 10 percent H_2SO_4. This capacity is lower than previous work has indicated; Squires (1986) reported that this was because the resin performance was being optimized for selenium removal rather than for boron removal.

MOLYBDENUM REMOVAL

At the pH value, redox condition, and iron content of agricultural drainage water, molybdenum is likely to be present in the hexavalent oxidation state as the monomeric tetrahedral oxyanion, molybdate, MoO_4^{2-}. At typical pH values and iron levels MoO_4^{2-} will be entirely dissolved.

Dannenberg et al. (1982) conducted laboratory-scale continuous-flow experiments on molybdenum (MoO_4^{2-}) removal from simulated molybdenum mine-concentrator waste. The treatment process utilized ferric sulfate addition to the waste adjusted to pH 4.2-5.0 with either lime or sulfuric acid

followed by one quiescent, then one mixed flocculation basin. A recycle dissolved air flotation (DAF) system was used for ferric precipitate removal. Molybdenum removal was by association (mechanism unknown, but could be adsorption, coprecipitation, or entrapment) with the ferric hydroxide floc. Molybdenum removal was dependent on the initial iron to molybdenum ratio. The lowest soluble molybdenum levels achieved were approximately 100 ug/L using an Fe/Mo dose of 9/1 from an initial concentration of 4 mg Mo/L. The effluent contained low dissolved iron levels (0.1 mg/L), but total iron was on the order of 7 mg/L.

Similar results were obtained by Ramadorai (1978) for molybdenum mining wastes with molybdenum reductions from 2-4 mg Mo/L to 1 mg/L and from 7-10 mg Mo/L to 2 mg/L at optimum pH values of 3-4 and Fe/Mo dose ratios of 6-10. DAF treatment with a surfactant added to aid flotation was used for precipitate removal. The possibility of needing DAF effluent filtration to meet iron and suspended solids discharge levels was raised. LeGendre and Runnells (1975) indicated that Fe/Mo doses of >10 and a pH optimum of 4.5 were required to remove 95 percent of dissolved molybdenum from mining wastes containing 1-11 mg/Mo/L. These waters also showed that the same removals that occurred in the molybdenum removal processes also took place in receiving streams polluted with acidic drainage from mines containing iron and molybdenum. Where the pH of the stream was depressed to 3.5 in the presence of Fe, the Mo and Fe contents of the sediments increased markedly.

Ion exchange using an amine-type weak base ion exchange resin (e.g., Amberlite XE299) at pH 3-4 in the bisulfite or chloride form has been employed for removing molybdenum from mining wastes. Field scale resin loadings of 3.66 lb Mo/ft^3 resin produced an effluent molybdenum concentration of 2 mg Mo/L from influent levels of 2-24 mg Mo/L (Ramadorai, 1978).

SUMMARY

Jenkins summarized his technology assessment for the treatment of selenium, boron, and molybdenum in drainage and presented recommendations for future work, as follows:

Selenium

1. The agricultural drainage wastewater of the San Joaquin Valley is a very difficult matrix from which to remove selenium because: (a) The selenium is present largely as the highly soluble selenate ion; (b) this ion is present together with a relatively massive background level of the chemically similar sulfate ion; and (c) significant levels of nitrate are present that must be removed before biologically mediated selenate reductions can be achieved.
2. Methods employing only chemical precipitation, adsorption, or ion exchange are not suitable for removal of selenate from the wastewater to the 2-5 ug/L levels contemplated for impounded waters.
3. The use of algae ponds for removal of selenate from these wastewaters to the levels required (2-5 ug/L) appears to be

unfeasible since the biological uptake of selenium is limited. Selenium reduction with digested algal materials is under study.

4. The only chemical equilibria that allow a sufficient distinction in properties between selenate and sulfate upon which to base a specific selenium removal technology appear to be the redox equilibria. Therefore, processes involving selenate reduction bear the most promise.
5. The Harza process, using beds of iron filings in pilot testing at the Panoche Drainage District, demonstrated selenium removal, although at low waste application rates and with significant column cementation problems. Prior to the considered scale-up of this process, laboratory-scale investigations of the mechanism should be completed. Alternative reactor configurations may well lead to increases in waste application rates.
6. Chemical methods for reducing selenate using reductants known to function at high concentrations and high temperatures should be investigated for their efficacy at the low selenate levels, and in the chemical matrix typical of agricultural drainage wastewater. Such methods include the use of sulfide, sulfur dioxide, and sulfur.
7. The microbial reduction of selenate to a variety of reduced selenium forms (e.g., selenite, selenium compounds, selenide, selenium metal, and organic selenium compounds) is claimed by pilot plant experiments at Murrieta Farms. The plant uses a

series of anaerobic reactors dosed with a degradable carbon source and followed by filtration and boron ion exchange units.

8. The microbial reduction process should use anaerobic reactor packing materials other than rocks, which have previously been demonstrated to be plagued by solids clogging and hydraulic flow distribution problems in denitrification reactors operated on this type of wastewater. The use of fixed bed (plastic), fluidized bed, and suspended growth reactors should be studied. The process should be examined for its feasibility in removing selenium from the highly saline evaporation pond contents, with the objective of deselenifying the contents of these ponds to "nonhazardous" levels.

Boron

1. The only current feasible technique for boron removal is the use of a selective ion exchange resin. This technique is already in commercial use in the removal of boron from magnesium chloride brines. Its use for the desired boron removal from San Joaquin Valley agricultural drainage wastewater has been successfully demonstrated on a pilot plant scale. The boron-selective resin appears to have some capacity for selenium removal.

Molybdenum

1. Molybdenum removal methods have not been evaluated on either the type of wastewater encountered or for the residual levels required in the San Joaquin Valley. Molybdenum removal techniques have

been developed for molybdenum-mining and mineral-processing wastewaters. These methods employ either precipitation/adsorption with ferric hydroxide at low pH or selective ion exchange.

2. Investigation is needed on the levels of molybdenum in agricultural drainage wastewater and on removal methods at these levels to produce the desired residual molybdenum concentrations.

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APPENDIX B

DESALINATION

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APPENDIX B
DESALINATION

INTRODUCTION

Desalination or desalting of drainage water can produce the highest quality product water. The process reduces salinity or TDS, as well as trace elements, and thereby renders the treated water usable for the widest range of reuse. In effect, desalination provides the most options for total water management. On the other hand, desalination is also expensive, as seen in table B-1, where different seawater conversion processes were evaluated for energy requirements and comparative costs by Concentration Specialists Inc. (1976). This section provides information to aid in evaluating desalination as part of the overall solution of the drainage problem.

DESALINATION PROCESSES

A number of major desalination processes are commonly used in wastewater reclamation. PRC Toups (1982) described six processes in a technical report to the Office of Water Research and Technology. These include: electrodialysis, evaporation, freezing, ion exchange, ultrafiltration, and reverse osmosis (RO).

Electrodialysis (ED) is an electrochemical process whereby the concentration of ionized salts or minerals in a water solution is reduced by alternate placement of positively and negatively charged permeable membranes across an electrical path (PRC Toups, 1982). These membranes selectively transfer either positively or negatively charged ions in the

Table B-1. Process Comparison, 100,000 Gal/d Seawater - 50 Percent Conversion

Process	kWh/1,000 gal	BTU Elec. (lb of Water)	BTU Steam (lb of Water)	BTU Fuel (lb of Water)	Energy Cost ($/yr)	Produce Water Energy Cost ($/AF)
Absorption Freezing-Vapor Compression (AFVC) (Direct Melting)	43	17	-	51	$56,800	1,014
Absorption Freezing-Vapor Compression (AFVC) (Indirect Melting)	48	20	-	55	59,400	1,061
Vacuum Freezing-Vapor Compression	45	18	-	49	59,400	1,061
Secondary Refrigerant (Direct Melting)	50	20	-	55	66,000	1,178
Secondary Refrigerant (Indirect Melting)	60	25	-	66	79,200	1,414
Vacuum Freezing-Ejector Absorption	14	6	71	104	132,000	2,357
Absorption (1 Effect Regeneration)	14	6	166	223	263,000	4,696
Vapor Compression	70	29	-	76	92,400	1,652
3 Effect Evaporator	6	2	400	507	566,000	10,107
6 Effect Evaporator	9	4	200	274	313,000	5,589
12 Effect Evaporator	12	5	100	138	168,000	1,786

(1) Energy cost taken as $0.04/kWh and $4 per 10^6 BTU steam.

Source: Concentration Specialists (1965).

solution such that in the alternating spaces between the membranes, salinity decreases in one space and increases in the next.

ED is presently one of the most effective means for desalting water containing TDS in the 1,000 to 3,000 mg/L range. The product water is generally desalted to less than 500 mg/L of TDS, usually through a multistage process using a series of modules. Typical salt removal ranges from 25 to 65 percent for each stage. The raw feedwater generally needs the same pretreatment as most membrane desalting processes; the water must be free of suspended solids and fouling substances. Membrane fouling and scaling must be minimized for effective operation. The precipitation of organic materials (e.g., proteins, amino acids) and salts (e.g., $CaSO_4$) requires pretreatment.

ED cost has two main components--pretreatment and desalination and the process is considered expensive. Tables B-2 and B-3 show, respectively, feedwater quality and ED desalting costs compiled by PRC Toups. Average drainwater quality in the San Luis Drain is summarized in table B-2 to compare the relative quality of San Luis Drain drain water to other desalted brackish feedwater using the ED process. The drain water is of significantly inferior quality, so it follows that both the pretreatment and desalting costs would be substantially higher to treat San Joaquin Valley drainage water, resulting in unit costs much higher than those cited in table B-3. Table B-3 reveals two other cost-increasing factors: (1) Table B-3 reflects costs 8 years ago and not the present higher costs, and (2) ED is a high-energy demanding process, but table B-3

Table B-2. Chemical Composition of Typical Brackish Waters[a]

Chemical Composition[b]	Brackish Waters				SLD*
	Type 1	Type 2	Type 3	Type 4	
Sodium	886	125	630	900	2,820
Calcium	118	316	116	250	714
Magnesium	72	69	15	70	270
Chloride	131	67	1,054	1,450	1,480
Sulfate	1,943	900	115	590	4,730
Bicarbonate	473	357	78	210	
Total Hardness as $CaCO_3$	590	1,073	354	912	
Manganese	1	0.10	Nil	0.1	.025
Fluoride			2		
Iron	2	1.0	0	0.4	0.11
Potassium	16	13	0	5	6
Nitrate	6.3	19	9	1	48
Silicate			17		37
Total Dissolved Solids	3,648	1,800	2,076	3,475	9,820
pH, units	7.6	7.9	8.1	7.3	8.2
Temp, °F	70	70	70	70	67
COD	10	7.9		7	32

[a]This data should be compared with qualities of wastewaters after pretreament.

[b]Expressed as mg/L unless otherwise noted.

Source: Larson and Leitner, 1979

*Average values in San Luis Drain at Mendota.

Table B-3. Brackish Water Desalting Costs: Electrodialysis Plants[a]

Item	Feedwater Type 1	2	3	4
Direct Capital Cost				
1. Installed Equipment Cost	1,040	920	740	920
2. Site Development	125	125	125	125
3. Intakes and Outfalls	75	75	75	75
4. Electric Utilities and Switchgear	125	80	80	125
Total Direct Capital Cost	1,365	1,200	1,020	1,245
Indirect Capital Cost				
5. Interest During Construction and Startup	24.7	21.8	17.6	21.8
6. Working Capital	68.2	60.0	51.0	62.2
7. Contingency - A&E Fee	233.3	205.1	174.2	212.6
Total Capital Cost	1,691.2	1,486.9	1,262.8	1,541.6
Operating Costs (Annual)				
8. Operating and Maintenance Labor	27.5	27.5	27.5	27.5
9. G&A @ 40%	11.0	11.0	11.0	11.0
10. Chemicals	3.5	3.5	3.5	3.5
11. Filters	10.4	10.4	10.4	10.4
12. Other Materials	5.2	4.6	3.7	4.6
13. Electricity @ $0.025 kWh	95.2	53.6	64.9	119.4
14. Membrane Replacement	27.8	24.6	19.8	24.6
Total Operating Costs	180.6	135.2	140.8	201.0
15. Fixed Charge @ 16.5%	279.0	245.3	208.4	254.4
Total Annual Cost	459.6	380.5	349.2	455.4
Water Cost, $/Kgal	1.32	1.10	1.00	1.31
Water Cost, $/AF	430	359	326	427

[a]All costs in 1979 first quarter dollars.

Source: Larson and Leitner, (1979)

was based on electricity costing only $.025 kWh rather than a more realistic $.075/kWh, a three-times greater cost.

Evaporation involves separating water from the dissolved minerals by volatilization and condensation of the water. The basic two-step distillation process involves evaporation and condensation and requires substantial energy. Table B-4 shows water costs reported by PRC Toups for a multistage flash and vertical evaporation system. These are costs exclusive of pretreatment, which is required to minimize scaling, and waste stream disposal. According to table B-4, vertical tube evaporators, the less costly of the two, produce water at about $2.40/Kgal or $782/acre-foot for a 1 Mgal/d plant. However, the process requires much energy, so the present cost could conceivably be three times higher. Desalting by evaporation is costly.

Vapor compression distillation is another evaporation desalting system. In this process, pure water vapor, which has been evaporated at a tube surface or in a flash chamber, is mechanically compressed to raise the pressure and temperature to further vaporize more water (Toups, 1982). Mechanical or electrical energy rather than heat is the primary energy source for distillation. This process has been studied by California DWR at their desalting system at Los Banos to obtain brine for their solar ponds. Findings of their studies are currently under preparation.

Freezing works on the principle that when a crystal is formed from a water solution the crystal is pure water, free of all impurities or minerals contained in the water solution. As more pure crystals form, the remaining solution becomes more and more concentrated. Toups (1982)

Table B-4. Water Costs - Desalting by Oil-Fired Distillation

Capacity (Mgal)	Multistage Flash		Vertical Tube Evaporators	
	$/Kgal	$/AF	$/Kgal	$/AF
1	6.41	2,090	5.90	1,923
3	4.98	1,623	4.24	1,382
5	4.44	1,447	3.96	1,291
10	3.93	1,281	3.28	1,069
30	3.43	1,118	2.82	919
50	3.15	1,027	2.62	854
100	2.86	932	2.40	782

Source: (Larson and Leitner 1979)

reported that at present no full-scale commercial plant is desalting water by freezing.

This process requires less energy than evaporation. Still, it requires considerable energy and is also very expensive. Table B-4 appears in the Toups' report. A column has been added to show the energy cost per acre-foot of product water (based on 50 percent conversion). The cost of desalting by freezing is clearly too costly.

Ion exchange (IX) involves the exchange of ions in a solution to the surface of a solid for ions of similar charge in which the solid is immersed (Toups, 1982). The medium involved in the exchange of ions is known as a resin, which consists of insoluble solids containing fixed cations or anions capable of reversible exchange with mobile ions of the opposite charge in the solution. Ion exchange can concentrate a material into a small volume or remove an undesirable constituent.

Pretreatment of IX feedwater is very important to achieve overall efficiency. Resin fouling and bed matting by suspended solids and colloidal matter need to be prevented. Traces of oil and gas in the feed solution can also cause operational problems. The resin should be protected from chemical and/or physical degradation. Toups reported that reliable, current cost data on IX are difficult to find in the literature. Generally, manufactured IX units are purchased and installed requiring only a foundation and water and electrical hookups.

Rohm and Haas has developed a new deionization technique called the Desal Process, which is reported to be economically competitive. Its application range is approximately 500 to 5,000 mg/L, TDS. Its main

advantage is that weak acid and base resins are used; thus the regeneration efficiency is essentially 100 percent, minimizing the regeneration costs as compared to conventional IX processes. However, all of the normal precautions with the general use of IX resins, including some added precautions, are applicable to the Desal Process.

Ultrafiltration (UF) is a membrane process that separates small particulates and high-molecular-weight organics from wastewater (Toups 1982). The process depends on a pressure-driving force and a membrane that is permeable to some constituents and impermeable to others. It differs from reverse osmosis in that UF membranes do not reject inorganic salts. Osmotic pressure need not be overcome, and UF systems can operate at low pressures of 5 to 100 lb/in^2. The main applications are for separation of macromolecular solutions and possibly pretreatment for RO. The UF process is therefore apparently not well suited for the desalting of drainage water. In the treatment results reported by Toups, only about 20 percent of the TDS was removed by UF.

Reverse Osmosis (RO) provides a wide range of separation capability for biological matter, colloidal materials, and many dissolved organic and inorganic solids (Toups, 1982). It uses a semipermeable membrane to separate water from dissolved salts and other material in solution or suspension. Pressure is applied to the saline feedwater. Water is forced through the membrane, and the salts remain behind in a more concentrated form. The membranes have various configurations. Figure B-1 shows a typical spiral-wound membrane configuration.

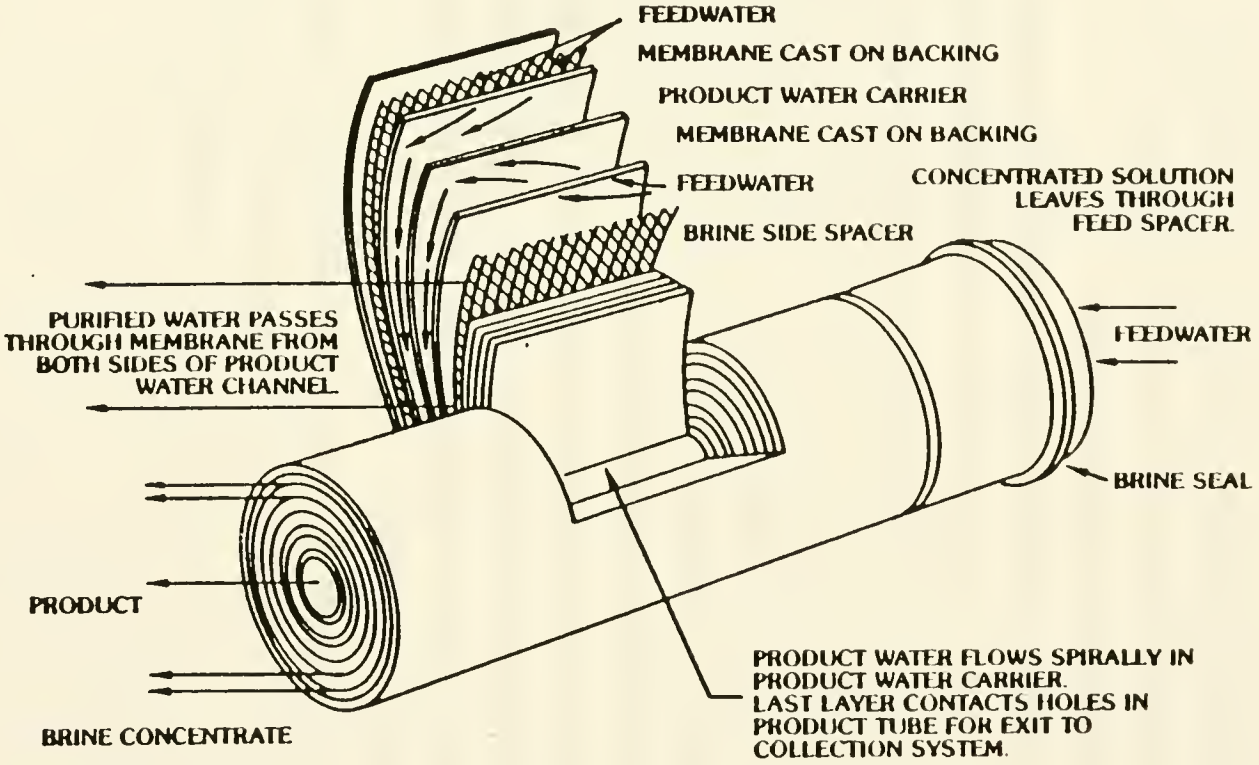
FEEDWATER
MEMBRANE CAST ON BACKING
PRODUCT WATER CARRIER
MEMBRANE CAST ON BACKING
FEEDWATER
BRINE SIDE SPACER
CONCENTRATED SOLUTION LEAVES THROUGH FEED SPACER.
PURIFIED WATER PASSES THROUGH MEMBRANE FROM BOTH SIDES OF PRODUCT WATER CHANNEL.
FEEDWATER
BRINE SEAL
PRODUCT
PRODUCT WATER FLOWS SPIRALLY IN PRODUCT WATER CARRIER. LAST LAYER CONTACTS HOLES IN PRODUCT TUBE FOR EXIT TO COLLECTION SYSTEM.
BRINE CONCENTRATE

FIGURE B-1. SPIRAL WOUND MEMBRANE CONFIGURATION

Pretreatment of the feedwater to minimize membrane fouling is essential for effective RO operation. Fouling occurs when various materials deposit on membranes or elsewhere in the RO module. The five main types of fouling are: (1) Membrane scaling, (2) fouling by metal oxides, (3) device plugging, (4) colloidal fouling, and (5) biological fouling. Membrane fouling can be reduced by proper filtration and pretreatment of the feedwater.

When treating drainage water, membrane scaling is a major problem to be avoided. As the RO process removes the product water from the feedwater, the residual brine concentrates and the solubility limits of some solutes may be exceeded. Salts, most commonly calcium carbonate and calcium sulfate, could precipitate on the membrane surfaces. Magnesium hydroxide, strontium sulfate, and silica also cause scaling. There are various pretreatment methods to minimize these problems.

In the RO process, recovery rate, i.e., the total product waterflow divided by the raw feedwater flow, is important. It affects the degree of membrane flushing as well as the salinity of both the reject and product water streams. A high recovery rate produces a small reject stream, while a low recovery rate produces a large reject stream. RO systems usually operate in the 50 to 90 percent range of recovery rate accomplished in stages. Each stage nominally recovers up to 50 percent of the volume treated. Recovery increases with the number of stages, but the cost also increases.

Toups (1982) reported that for a 1 Mgal/d RO plant treating 2,000-10,000 mg/L, TDS, feedwater, the product water costs about

$1.38/1,000 gal or $450/acre-foot (product water TDS was not reported). This cost, however, is not considered applicable to treatment of drainage water in the valley because there are too many unknowns about the bases on which the cost was derived by Toups, e.g., what is the chemical composition of the feedwater? What was the required pretreatment? What was the cost of energy? Is wastestream disposal included?, etc.

This review of desalination processes provides background for the basic premise that most methods are too costly for agricultural drainage water treatment. Desalination methods are energy intensive and result in a high volume of salt, which must be disposed of either within the San Joaquin Valley or exported outside to acceptable disposal areas.

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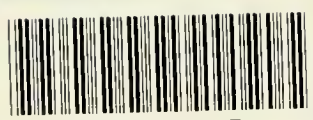
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